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8235 8241 8248 8254 1 1 2 3 3 4 5 5 6 67 8261 8267 8274 8280 8287 8293 8299 8306 8312 8319 1 1 2 3 3 4 5 5 6 68 8325 8331 8338 8344 8351 8357 8363 8370 8376 8382 1 1 2 3 3 4 4 5 6 69 8388 8395 8401 8407 8414 8420 8426 8432 8439 8445 1 1 2 2 3 4 4 5 6 70 8451 8457 8463 8470 8476 8482 8488 8494 8500 8506 1 1 2 2 3 4 4 5 6 71 8513 8519 8525 8531 8537 8543 8549 8555 8561 8567 1 1 2 2 3 4 4 5 5 72 8573 8579 8585 8591 8597 8603 8609 8615 8621 8627 1 1 2 2 3 4 4 5 5 73 8633 8639 8645 8651 8657 8663 8669 8675 8681 8686 1 1 2 2 3 4 4 5 5 74 8692 8698 8704 8710 8716 8722 8727 8733 8739 8745 1 1 2 2 3 4 4 5 5 75 8751 8756 8762 8768 8774 8779 8785 8791 8797 8802 1 1 2 2 3 3 4 5 5 76 8808 8814 8820 8825 8831 8837 8842 8848 8854 8859 1 1 2 2 3 3 4 5 5 77 8865 8871 8876 8882 8887 8893 8899 8904 8910 8915 1 1 2 2 3 3 4 4 5 78 8921 8927 8932 8938 8943 8949 8954 8960 8965 8971 1 1 2 2 3 3 4 4 5 79 8976 8982 8987 8993 8998 9004 9009 9015 9020 9025 1 1 2 2 3 3 4 4 5 80 9031 9036 9042 9047 9053 9058 9063 9069 9074 9079 1 1 2 2 3 3 4 4 5 81 9085 9090 9096 9101 9106 9112 9117 9122 9128 9133 1 1 2 2 3 3 4 4 5 82 9138 9143 9149 9154 9159 9165 9170 9175 9180 9186 1 1 2 2 3 3 4 4 5 83 9191 9196 9201 9206 9212 9217 9222 9227 9232 9238 1 1 2 2 3 3 4 4 5 84 9243 9248 9253 9258 9263 9269 9274 9279 9284 9289 1 1 2 2 3 3 4 4 5 85 9294 9299 9304 9309 9315 9320 9325 9330 9335 9340 1 1 2 2 3 3 4 4 5 86 9345 9350 9355 9360 9365 9370 9375 9380 9385 9390 1 1 2 2 3 3 4 4 5 87 9395 9400 9405 9410 9415 9420 9425 9430 9435 9440 0 1 1 2 2 3 3 4 4 88 9445 9450 9455 9460 9465 9469 9474 9479 9484 9489 0 1 1 2 2 3 3 4 4 89 9494 9499 9504 9509 9513 9518 9523 9528 9533 9538 0 1 1 2 2 3 3 4 4 90 9542 9547 9552 9557 9562 9566 9571 9576 9581 9586 0 1 1 2 2 3 3 4 4 91 9590 9595 9600 9605 9609 9614 9619 9624 9628 9633 0 1 1 2 2 3 3 4 4 92 9638 9643 9647 9652 9657 9661 9666 9671 9675 9680 0 1 1 2 2 3 3 4 4 93 9685 9689 9694 9699 9703 9708 9713 9717 9722 9727 0 1 1 2 2 3 3 4 4 94 9731 9736 9741 9745 9750 9754 9759 9763 9768 9773 0 1 1 2 2 3 3 4 4 95 9777 9782 9786 9791 9795 9800 9805 9809 9814 9818 0 1 1 2 2 3 3 4 4 96 9823 9827 9832 9836 9841 9845 9850 9854 9859 9863 0 1 1 2 2 3 3 4 4 97 9868 9872 9877 9881 9886 9890 9894 9899 9903 9908 0 1 1 2 2 3 3 4 4 98 9912 9917 9921 9926 9930 9934 9939 9943 9948 9952 0 1 1 2 2 3 3 4 4 99 9956 9961 9965 9969 9974 9978 9983 9987 9997 9996 0 1 1 2 2 3 3 4

AntiLogarithms N 0 1 2 3 4 5 6 7 8 9 1 2 3 4 5 6 7 8 9 00 1000 1002 1005 1007 1009 1012 1014 1016 1019 1021 0 0 1 1 1 1 2 2 2 .01 1023 1026 1028 1030 1033 1035 1038 1040 1042 1045 0 0 1 1 1 1 2 2 2 .02 1047 1050 1052 1054 1057 1059 1062 1064 1067 1069 0 0 1 1 1 1 2 2 2 .03 1072 1074 1076 1079 1081 1084 1086 1089 1091 1094 0 0 1 1 1 1 2 2 2 .04 1096 1099 1102 1104 1107 1109 1112 1114 1117 1119 0 1 1 1 1 2 2 2 2 .05 1122 1125 1127 1130 1132 1135 1138 1140 1143 1146 0 1 1 1 1 2 2 2 2 .06 1148 1151 1153 1156 1159 1161 1164 1167 1169 1172 0 1 1 1 1 2 2 2 2 .07 1175 1178 1180 1183 1186 1189 1191 1194 1197 1199 0 1 1 1 1 2 2 2 2 .08 1202 1205 1208 1211 1213 1216 1219 1222 1225 1227 0 1 1 1 1 2 2 2 3 .09 1230 1233 1236 1239 1242 1245 1247 1250 1253 1256 0 1 1 1 1 2 2 2 3 .10 1259 1262 1265 1268 1271 1274 1276 1279 1282 1285 0 1 1 1 1 2 2 2 3 .11 1288 1291 1294 1297 1300 1303 1306 1309 1312 1315 0 1 1 1 2 2 2 2 3 .12 1318 1321 1324 1327 1330 1334 1337 1340 1343 1346 0 1 1 1 2 2 2 2 3 .13 1349 1352 1355 1358 1361 1365 1368 1371 1374 1377 0 1 1 1 2 2 2 3 3 .14 1380 1384 1387 1390 1393 1396 1400 1403 1406 1409 0 1 1 1 2 2 2 3 3 .15 1413 1416 1419 1422 1426 1429 1432 1435 1439 1442 0 1 1 1 2 2 2 3 3 .16 1445 1449 1452 1455 1459 1462 1466 1469 1472 1476 0 1 1 1 2 2 2 3 3 .17 1479 1483 1486 1489 1493 1496 1500 1503 1507 1510 0 1 1 1 2 2 2 3 3 .18 1514 1517 1521 1524 1528 1531 1535 1538 1542 1545 0 1 1 1 2 2 2 3 3 .19 1549 1552 1556 1560 1563 1567 1570 1574 1578 1581 0 1 1 1 2 2 3 3 3 .20 1585 1589 1592 1596 1600 1603 1607 1611 1614 1618 0 1 1 1 2 2 3 3 3 .21 1622 1626 1629 1633 1637 1641 1644 1648 1652 1656 0 1 1 2 2 2 3 3 3 .22 1660 1663 1667 1671 1675 1679 1683 1687 1690 1694 0 1 1 2 2 2 3 3 3 .23 1698 1702 1706 1710 1714 1718 1722 1726 1730 1734 0 1 1 2 2 2 3 3 4 .24 1738 1742 1746 1750 1754 1758 1762 1766 1770 1774 0 1 1 2 2 2 3 3 4 .25 1778 1782 1786 1791 1795 1799 1803 1807 1811 1816 0 1 1 2 2 2 3 3 4 .26 1820 1824 1828 1832 1837 1841 1845 1849 1854 1858 0 1 1 2 2 3 3 3 4 .27 1862 1866 1871 1875 1879 1884 1888 1892 1897 1901 0 1 1 2 2 3 3 3 4 .28 1905 1910 1914 1919 1923 1928 1932 1936 1941 1945 0 1 1 2 2 3 3 4

4 .29 1950 1954 1959 1963 1968 1972 1977 1982 1986 1991 0 1 1 2 2 3 3 4 4 .30 1995 2000 2004 2009 2014 2018 2023 2028 2032 2037 0 1 1 2 2 3 3 4 4 .31 2042 2046 2051 2056 2061 2065 2070 2075 2080 2084 0 1 1 2 2 3 3 4 4 .32 2089 2094 2099 2104 2109 2113 2118 2123 2128 2133 0 1 1 2 2 3 3 4 4 .33 2138 2143 2148 2153 2158 2163 2168 2173 2178 2183 0 1 1 2 2 3 3 4 4 .34 2188 2193 2198 2203 2208 2213 2218 2223 2228 2234 1 1 2 2 3 3 4 4 5 .35 2239 2244 2249 2254 2259 2265 2270 2275 2280 2286 1 1 2 2 3 3 4 4 5 .36 2291 2296 2301 2307 2312 2317 2323 2328 2333 2339 1 1 2 2 3 3 4 4 5 .37 2344 2350 2355 2360 2366 2371 2377 2382 2388 2393 1 1 2 2 3 3 4 4 5 .38 2399 2404 2410 2415 2421 2427 2432 2438 2443 2449 1 1 2 2 3 3 4 4 5 .39 2455 2460 2466 2472 2477 2483 2489 2495 2500 2506 1 1 2 2 3 3 4 5 5 .40 2512 2518 2523 2529 2535 2541 2547 2553 2559 2564 1 1 2 2 3 4 4 5 5 .41 2570 2576 2582 2588 2594 2600 2606 2612 2618 2624 1 1 2 2 3 4 4 5 5 .42 2630 2636 2642 2649 2655 2661 2667 2673 2679 2685 1 1 2 3 4 4 5 6 .43 2692 2698 2704 2710 2716 2723 2729 2735 2742 2748 1 1 2 3 3 4 4 5 6 .44 2754 2761 2767 2773 2780 2786 2793 2799 2805 2812 1 1 2 3 3 4 4 5 6 .45 2818 2825 2831 2838 2844 2851 2858 2864 2871 2877 1 1 2 3 3 4 5 5 6 .46 2884 2891 2897 2904 2911 2917 2924 2931 2938 2944 1 1 2 3 3 4 5 5 6 .47 2951 2958 2965 2972 2979 2985 2992 2999 3006 3013 1 1 2 3 3 4 5 5 6 .48 3020 3027 3034 3041 3048 3055 3062 3069 3076 3083 1 1 2 3 3 4 5 6 6 .49 3090 3097 3105 3112 3119 3126 3133 3141 3148 3155 1 1 2 3 3 4 5 6 6 Table II Rationalised 2023-24 Table II (Continued) N 0 1 2 3 4 5 6 7 8 9 1 2 3 4 5 6 7 8 9 .50 3162 3170 3177 3184 3192 3199 3206 3214 3221 3228 1 1 2 3 4 4 5 6 7 .51 3236 3243 3251 3258 3266 3273 3281 3289 3296 3304 1 2 2 3 4 5 5 6 7 .52 3311 3319 3327 3334 3342 3350 3357 3365 3373 3381 1 2 2 3 4 5 5 6 7 .53 3388 3396 3404 3412 3420 3428 3436 3443 3451 3459 1 2 2 3 4 5 6 6 7 .54 3467 3475 3483 3491 3499 3508 3516 3524 3532 3540 1 2 2 3 4 5 6 6 7 .55 3548 3556 3565 3573 3581 3589 3597 3606 3614 3622 1 2 2 3 4 5 6 7 7 .56 3631 3639 3648 3656 3664 3673 3681 3690 3698 3707 1 2 3 3 4 5 6 7 8 .57 3715 3724 3733 3741 3750 3758 3767 3776 3784 3793 1 2 3 3 4 5 6 7 8 .58 3802 3811 3819 3828 3837 3846 3855 3864 3873 3882 1 2 3 4 4 5 6 7 8 .59 3890 3899 3908 3917 3926 3936 3945 3954 3963 3972 1 2 3 4 5 5 6 7 8 .60 3981 3990 3999 4009 4018 4027 4036 4046 4055 4064 1 2 3 4 5 6 6 7 8 .61 4074 4083 4093 4102 4111 4121 4130 4140 4150 4159 1 2 3 4 5 6 7 8 9 .62 4169 4178 4188 4198 4207 4217 4227 4236 4246 42S6 1 2 3 4 5 6 7 8 9 .63 4266 4276 4285 4295 4305 4315 4325 4335 4345 4355 1 2 3 4 5 6 7 8 9 .64 4365 4375 4385 4395 4406 4416 4426 4436 4446 4457 1 2 3 4 5 6 7 8 9 .65 4467 4477 4487 4498 4508 4519 4529 4539 4550 4560 1 2 3 4 5 6 7 8 9 .66 4571 4581 4592 4603 4613 4624 4634 4645 4656 4667 1 2 3 4 5 6 7 9 10 .67 4677 4688 4699 4710 4721 4732 4742 4753 4764 4775 1 2 3 4 5 7 8 9 10 .68 4786 4797 4808 4819 4831 4842 4853 4864 4875 4887 1 2 3 4 6 7 8 9 10 .69 4898 4909 4920 4932 4943 4955 4966 4977 4989 5000 1 2 3 5 6 7 8 9 10 .70 5012 5023 5035 5047 5058 5070 5082 5093 5105 5117 1 2 4 5 6 7 8 9 11 .71 5129 5140 5152 5164 5176 5188 5200 5212 5224 5236 1 2 4 5 6 7 8 10 11 .72 5248 5260 5272 5284 5297 5309 5321 5333 5346 5358 1 2 4 5 6 7 9 10 11 .73 5370 5383 5395 5408 5420 5433 5445 5458 5470 5483 1 3 4 5 6 8 9 10 11 .74 5495 5508 5521 5534 5546 5559 5572 5585 5598 5610 1 3 4 5 6 8 9 10 12 .75 5623 5636 5649 5662 5675 5689 5702 5715 5728 5741 1 3 4 5 7 8 9 10 12 .76 5754 5768 5781 5794 5808 5821 5834 5848 5861 5875 1 3 4 5 7 8 9 11 12 .77 5888 5902 5916 5929 5943 5957 5970 5984 5998 6012 1 3 4 5 7 8 10 11 12 .78 6026 6039 6053 6067 6081 6095 6109 6124 6138 6152 1 3 4 6 7 8 10 11 13 .79 6166 6180 6194 6209 6223 6237 6252 6266 6281 6295 1 3 4 6 7 9 10 11 13 .80 6310 6324 6339 6353 6368 6383 6397 6412 6427 6442 1 3 4 6 7 9 10 12 13 .81 6457 6471 6486 6501 6516 6531 6546 6561 6577 6592 2 3 5 6 8 9 11 12 14 .82 6607 6622 6637 6653 6668 6683 6699 6714 6730 6745 2 3 5 6 8 9 11 12 14 .83 6761 6776 6792 6808 6823 6839 6855 6871 6887 6902 2 3 5 6 8 9 11 1314 .84 6918 6934 6950 6966 6982 6998 7015 7031 7047 7063 2 3 5 6 8 10 11 13 15 .85 7079 7096 7112 7129 7145 7161 7178 7194 7211 7228 2 3 5 7 8 10 12 13 15 .86 7244 7261 7278 7295 7311 7328 7345 7362 7379 7396 2 3 5 7 8 10 12 13 15 .87 7413 7430 7447 7464 7482 7499 7516 7534 7551 7568 2 3 5 7 9 10 12 14 16 .88 7586 7603 7621 7638 7656 7674 7691 7709 7727 7745 2 4 5 7 9 11 12 14 16 .89 7762 7780 7798 7816 7834 7852 7870 7889 7907

7925 2 4 5 7 9 11 13 14 16 .90 7943 7962 7980 7998 8017 8035 8054 8072 8091 8110 2 4 6 7 9 11 13 15 17 .91 8128 8147 8166 8185 8204 8222 8241 8260 8279 8299 2 4 6 8 9 11 13 15 17 .92 8318 8337 8356 8375 8395 8414 8433 8453 8472 8492 2 4 6 8 10 12 14 15 17 .93 8511 8531 8551 8570 8590 8610 8630 8650 8670 8690 2 4 6 8 10 12 14 16 18 .94 8710 8730 8750 8770 8790 8810 8831 8851 8872 8892 2 4 6 8 10 12 14 16 18 .95 8913 8933 8954 8974 8995 9016 9036 9057 9078 9099 2 4 6 8 10 12 15 17 19 .96 9120 9141 9162 9183 9204 9226 9247 9268 9290 9311 2 4 6 8 11 13 15 17 19 .97 9333 9354 9376 9397 9419 9441 9462 9484 9506 9528 2 4 7 9 11 13 15 17 20 .98 9550 9572 9594 9616 9638 9661 9683 9705 9727 9750 2 4 7 9 11 13 16 18 20 .99 9772 9795 9817 9840 9863 9886 9908 9931 9954 9977 2 5 7 9 11 14 16 18 20 AntiLogarithms Rationalised 2023-24 Notes Rationalised 2023-24 Notes Rationalised 2023-24Appendices 215 Metre (m): The metre, symbol m, is the SI unit of length. It is defined by taking the fixed numerical value of the speed of light in vacuum c to be 299792458 when expressed in the unit ms-1, where the second is defined in terms of the caesium frequency. Kilogram (k): The kilogram, symbol kg, is the SI unit of mass. It is defined by taking the fixed numerical value of the planck constant h to be $6.62607015 \times 10^{-34}$ when expressed in the unit Js, which is equal to kgm2s-1, where the metre and the second are defined in terms of c and Vcs. Second (s): The symbol s, is the SI unit of time. It is defined by taking the fixed numerical value of the caesium frequency Vcs, the unperturbed ground-state hyperfine transition frequency of the caesium-133 atom, to be 9192631770 when expressed in the unit Hz, which is equal to s–1. Ampere (A): The ampere, symbol A, is the SI unit of electric current. It is defined by taking the fixed numerical value of the elementary charge e to be $1.602176634 \times 10^{-19}$ when expressed in the unit C, which is equal to A s, where the second is defined in terms of. Kelvin (K): The Kelvin, symbol K, is the SI unit of thermodynamic temperature. It is defined by taking the fixed numerical value of the Boltzmann constant K to be $1.380649 \times 10^{-23}$ when expressed in the unit JK–1, which is equal to kgm2s–2K–1, where the kilogram, metre and second are defined in terms of h, c and Vcs. Mole (mol): The mole, symbol mol, is the SI unit of amount of substance. One mole contains exactly $6.02214076 \times 10^{23}$ elementary entities. This number is the fixed numerical value of the Avogadro constant, NA, when expressed in the unit mol–1 and is called the Avogadro number. The amount of substance, symbol n, of a system is a measure of the number of specified elementary entities. An elementary entity may be an atom, a molecule, an ion, an electron, any other particle or specified group of particles. Candela (cd): The candela, symbol cd is the SI unit of luminous intensity in a given direction. It is defined by taking the fixed numerical value of the luminous efficacy of monochromatic radiation of frequency $540 \times 10^{12}$ Hz, Kcd, to be 683 when expressed in the unit lm·W–1, which is equal to cd·sr·W–1, or cd sr kg–1m–2s3, where the kilogram, metre and second are defined in terms of h, c and Vcs. (The symbols listed here are internationally agreed and should not be changed in other languages and scripts. Definitions of the SI Base Units Appendix I Rationalised 2023-24 216 chemistry Element Symbol Atomic Molar Number mass/ (g mol–1) Actinium Ac 89 227.03 Aluminium Al 13 26.98 Americium Am 95 (243) Antimony Sb 51 121.75 Argon Ar 18 39.95 Arsenic As 33 74.92 Astatine At 85   210 Barium Ba 56 137.34 Berkelium Bk 97 (247) Beryllium Be 4 9.01 Bismuth Bi 83 208.98 Bohrium Bh 107 (264) Boron B 5 10.81 Bromine Br 35 79.91 Cadmium Cd 48 112.40 Caesium Cs 55 132.91 Calcium Ca 20 40.08 Californium Cf 98 251.08 Carbon C 6 12.01 Cerium Ce 58 140.12 Chlorine Cl 17 35.45 Chromium Cr 24 52.00 Cobalt Co 27 58.93 Copper Cu 29 63.54 Curium Cm 96 247.07 Dubnium Db 105 (263) Dysprosium Dy 66 162.50 Einsteinium Es 99 (252) Erbium Er 68 167.26 Europium Eu 63 151.96 Fermium Fm 100 (257.10) Fluorine F 9 19.00 Francium Fr 87 (223) Gadolinium Gd 64 157.25 Gallium Ga 31 69.72 Germanium Ge 32 72.61 Gold Au 79 196.97 Hafnium Hf 72 178.49 Hassium Hs 108 (269) Helium He 2 4.00 Holmium Ho 67 164.93 Hydrogen H 1 1.0079 Indium In 49 114.82 Iodine I 53 126.90 Iridium Ir 77 192.2 Iron Fe 26 55.85 Krypton Kr 36 83.80 Lanthanum La 57 138.91 Lawrencium Lr 103 (262.1) Lead Pb 82 207.19 Lithium Li 3 6.94 Lutetium Lu 71 174.96 Magnesium Mg 12 24.31 Manganese Mn 25 54.94 Meitneium Mt 109 (268) Mendelevium

Md 101 258.10 Mercury Hg 80 200.59 Molybdenum Mo 42 95.94 Neodymium Nd 60 144.24 Neon Ne 10 20.18 Neptunium Np 93 (237.05) Nickel Ni 28 58.71 Niobium Nb 41 92.91 Nitrogen N 7 14.0067 Nobelium No 102 (259) Osmium Os 76 190.2 Oxygen O 8 16.00 Palladium Pd 46 106.4 Phosphorus P 15 30.97 Platinum Pt 78 195.09 Plutonium Pu 94 (244) Polonium Po 84 210 Potassium K 19 39.10 Praseodymium Pr 59 140.91 Promethium Pm 61 (145) Protactinium Pa 91 231.04 Radium Ra 88 (226) Radon Rn 86 (222) Rhenium Re 75 186.2 Rhodium Rh 45 102.91 Rubidium Rb 37 85.47 Ruthenium Ru 44 101.07 Rutherfordium Rf 104 (261) Samarium Sm 62 150.35 Scandium Sc 21 44.96 Seaborgium Sg 106 (266) Selenium Se 34 78.96 Silicon Si 14 28.08 Silver Ag 47 107.87 Sodium Na 11 22.99 Strontium Sr 38 87.62 Sulphur S 16 32.06 Tantalum Ta 73 180.95 Technetium Tc 43 (98.91) Tellurium Te 52 127.60 Terbium Tb 65 158.92 Thallium Tl 81 204.37 Thorium Th 90 232.04 Thulium Tm 69 168.93 Tin Sn 50 118.69 Titanium Ti 22 47.88 Tungsten W 74 183.85 Ununbium Uub 112 (277) Ununnilium Uun 110 (269) Unununium Uuu 111 (272) Uranium U 92 238.03 Vanadium V 23 50.94 Xenon Xe 54 131.30 Ytterbium Yb 70 173.04 Yttrium Y 39 88.91 Zinc Zn 30 65.37 Zirconium Zr 40 91.22 Element Symbol Atomic Molar Number mass/ (g mol–1) The value given in parenthesis is the molar mass of the isotope of largest known half-life. Elements, their Atomic Number and Molar Mass Appendix II Rationalised 2023-24 Appendices 217 A. Specific and Molar Heat Capacities for Some Substances at 298 K and one Atmospheric Pressure Substance Specific Heat Capacity Molar Heat Capacity (J/g) (J/mol) air 0.720 20.8 water (liquid) 4.184 75.4 ammonia (gas) 2.06 35.1 hydrogen chloride 0.797 29.1 hydrogen bromide 0.360 29.1 ammonia (liquid) 4.70 79.9 ethyl alcohol (liquid) 2.46 113.16 ethylene glycol (liquid) 2.42 152.52 water (solid) 2.06 37.08 carbon tetrachloride (liquid) 0.861 132.59 chlorofluorocarbon ($CCl_2F_2$) 0.5980 72.35 ozone 0.817 39.2 neon 1.03 20.7 chlorine 0.477 33.8 bromine 0.473 75.6 iron 0.460 25.1 copper 0.385 24.7 aluminium 0.902 24.35 gold 0.128 25.2 graphite 0.720 8.65 B. Molar Heat Capacities for Some Gases (J/mol) Gas Cp Cv Cp - Cv Cp / Cv Monatomic* helium 20.9 12.8 8.28 1.63 argon 20.8 12.5 8.33 1.66 iodine 20.9 12.6 8.37 1.66 mercury 20.8 12.5 8.33 1.66 Diatomic† hydrogen 28.6 20.2 8.33 1.41 oxygen 29.1 20.8 8.33 1.39 nitrogen 29.0 20.7 8.30 1.40 hydrogen chloride 29.6 21.0 8.60 1.39 carbon monoxide 29.0 21.0 8.00 1.41 Triatomic† nitrous oxide 39.0 30.5 8.50 1.28 carbon dioxide 37.5 29.0 8.50 1.29 Polyatomic† ethane 53.2 44.6 8.60 1.19 *Translational kinetic energy only. †Translational, vibrational and rotational energy. Appendix III Rationalised 2023-24 218 chemistry Physical Constants Quantity Symbol Traditional Units SI Units Acceleration of gravity g 980.6 cm/s 9.806 m/s Atomic mass unit (1/12 amu 1.6606 × 10-24 g 1.6606 × 10-27 kg the mass of 12C atom) or u Avogadro constant NA 6.022 ×1023 6.022 × 1023 particles/mol particles/mol Bohr radius ao 0.52918 X 5.2918 × 10-11 m 5.2918 × 10-9 cm Boltzmann constant k 1.3807 × 10-16 erg/K 1.3807 × 10-23 J/K Charge-to-mass e/m 1.758820 ×l08 coulomb/g 1.7588 × 1011 C/kg ratio of electron Electronic charge e 1.602176 × 10-19 coulomb 1.60219 × 10-19 C 4.8033 × 10-19 esu Electron rest mass me 9.109382 ×10-28 g 9.10952 ×10-31 kg 0.00054859 u Faraday constant F 96,487 coulombs/eq 96,487 C/mol e23.06 kcal/volt. eq 96,487 J/V.mol eGas constant R 0.8206 L atm mol K 8.3145 kPa dm mol K 3 1.987 cal mol K 8.3145 J/mol.K Molar volume (STP) Vm 22.710981 L/mol 22.710981 × 10-3 m3/mol 22.710981 dm3/mol Neutron rest mass mn 1.674927 × 10-24 g 1.67495 × 10-27 kg 1.008665 u Planck constant h 6.6262 × 10-27 ergs 6.6262 × 10-34 J s Proton rest mass mp 1.6726216 ×10-24 g 1.6726 ×10-27 kg 1.007277 u Rydberg constant R∞ 3.289 × 1015 cycles/s 1.0974 × 107 m-1 2.1799 × 10-11 erg 2.1799 × 10-18 J Speed of light c 2.9979 ×1010 cm/s 2.9979 × 108 m/s (in a vacuum) (186,281 miles/second) π = 3.1416 2.303 R = 4.576 cal/mol K = 19.15 J/mol K e = 2.71828 2.303 RT (at 25°C) = 1364 cal/mol = 5709 J/mol ln X = 2.303 log X Appendix IV Rationalised 2023-24 Appendices 219 Common Unit of Mass and Weight 1 pound = 453.59 grams 1 pound = 453.59 grams = 0.45359 kilogram 1 kilogram = 1000 grams = 2.205 pounds 1 gram = 10 decigrams = 100 centigrams = 1000 milligrams 1 gram = 6.022 × 1023 atomic mass units or u 1 atomic mass unit = 1.6606 × 10–24 gram 1 metric tonne = 1000 kilograms = 2205 pounds Common Unit of Volume 1 quart = 0.9463 litre 1 litre = 1.056 quarts 1

litre = 1 cubic decimetre = 1000 cubic centimetres = 0.001 cubic metre 1 millilitre = 1 cubic centimetre = 0.001 litre = $1.056 \times 10^{-3}$ quart 1 cubic foot = 28.316 litres = 29.902 quarts = 7.475 gallons Common Units of Energy 1 joule = $1 \times 10^7$ ergs 1 thermochemical calorie** = 4.184 joules = $4.184 \times 10^7$ ergs = $4.129 \times 10^{-2}$ litre-atmospheres = $2.612 \times 10^{19}$ electron volts 1 ergs = $1 \times 10^{-7}$ joule = $2.3901 \times 10^{-8}$ calorie 1 electron volt = $1.6022 \times 10^{-19}$ joule = $1.6022 \times 10^{-12}$ erg = 96.487 kJ/mol† 1 litre-atmosphere = 24.217 calories = 101.32 joules = $1.0132 \times 10^9$ ergs 1 British thermal unit = 1055.06 joules = $1.05506 \times 10^{10}$ ergs = 252.2 calories Common Units of Length 1 inch = 2.54 centimetres (exactly) 1 mile = 5280 feet = 1.609 kilometres 1 yard = 36 inches = 0.9144 metre 1 metre = 100 centimetres = 39.37 inches = 3.281 feet = 1.094 yards 1 kilometre = 1000 metres = 1094 yards = 0.6215 mile 1 Angstrom = $1.0 \times 10^{-8}$ centimetre = 0.10 nanometre = $1.0 \times 10^{-10}$ metre = $3.937 \times 10^{-9}$ inch Common Units of Force* and Pressure 1 atmosphere = 760 millimetres of mercury = $1.013 \times 10^5$ pascals = 14.70 pounds per square inch 1 bar = $10^5$ pascals 1 torr = 1 millimetre of mercury 1 pascal = $1\ kg/ms^2$ = $1\ N/m^2$ Temperature SI Base Unit: Kelvin (K) K = -273.15° C K = ° C + 273.15 ° F = 1.8(° C) + 32 * Force: 1 newton (N) = 1 kg m/s², i.e., the force that, when applied for 1 second, gives a 1-kilogram mass a velocity of 1 metre per second. ** The amount of heat required to raise the temperature of one gram of water from 14.50C to 15.50C. † Note that the other units are per particle and must be multiplied by $6.022 \times 10^{23}$ to be strictly comparable. Some Useful Conversion Factors Appendix V Rationalised 2023-24 220 chemistry INORGANIC SUBSTANCES

Substance Enthalpy of formation, Gibbs Energy of formation, Entropy,* $\Delta f\ H^0$/ (kJ mol–1) $\Delta f\ G^0$/ (kJ mol–1) $S^0$/(J K–1 mol–1) Aluminium Al(s) 0 0 28.33 Al3+(aq) − 524.7 −481.2 −321.7 Al2O3(s) −1675.7 −1582.3 50.92 Al(OH)3(s) −1276 — — AlCl3(s) −704.2 −628.8 110.67 Antimony SbH3(g) 145.11 147.75 232.78 SbCl3(g) −313.8 −301.2 337.80 SbCl5(g) −394.34 −334.29 401.94 Arsenic As(s), gray 0 0 35.1 As2S3(s) −169.0 −168.6 163.6 AsO4 3–(aq) −888.14 −648.41 −162.8 Barium Ba(s) 0 0 62.8 Ba2+(aq) −537.64 −560.77 9.6 BaO(s) −553.5 −525.1 70.42 BaCO3(s) −1216.3 −1137.6 112.1 BaCO3(aq) −1214.78 −1088.59 −47.3 Boron B(s) 0 0 5.86 B2O3(s) −1272.8 −1193.7 53.97 BF3(g) −1137.0 −1120.3 254.12 Bromine Br2(l) 0 0 152.23 Br2(g) 30.91 3.11 245.46 Br(g) 111.88 82.40 175.02 Br− (aq) −121.55 −103.96 82.4 HBr(g) −36.40 −53.45 198.70 BrF3(g) −255.60 −229.43 292.53 Calcium Ca(s) 0 0 41.42 Ca(g) 178.2 144.3 154.88 Ca2+(aq) −542.83 −553.58 −53.1 (continued) Thermodynamic Data at 298 K Appendix VI Rationalised 2023-24 Appendices 221 Calcium (continued) CaO(s) −635.09 −604.03 39.75 Ca(OH)2(s) −986.09 −898.49 83.39 Ca(OH)2(aq) −1002.82 −868.07 −74.5 CaCO3(s), calcite −1206.92 −1128.8 92.9 CaCO3(s), aragonite −1207.1 −1127.8 88.7 CaCO3(aq) −1219.97 −1081.39 −110.0 CaF2(s) −1219.6 −1167.3 68.87 CaF2(aq) −1208.09 −1111.15 −80.8 CaCl2(s) −795.8 −748.1 104.6 CaCl2(aq) −877.1 −816.0 59.8 CaBr2(s) −682.8 −663.6 130 CaC2(s) −59.8 −64.9 69.96 CaS(s) −482.4 −477.4 56.5 CaSO4(s) −1434.11 −1321.79 106.7 CaSO4(aq) −1452.10 −1298.10 −33.1 Carbon** C(s), graphite 0 0 5.740 C(s), diamond 1.895 2.900 2.377 C(g) 716.68 671.26 158.10 CO(g) −110.53 −137.17 197.67 CO2(g) −393.51 −394.36 213.74 CO3 2–(aq) −677.14 −527.81 −56.9 CCl4(l) −135.44 −65.21 216.40 CS2(l) 89.70 65.27 151.34 HCN(g) 135.1 124.7 201.78 HCN(l) 108.87 124.97 112.84 Cerium Ce(s) 0 0 72.0 Ce3+(aq) −696.2 −672.0 −205 Ce4+(aq) −537.2 −503.8 −301 Chlorine Cl2(g) 0 0 223.07 Cl(g) 121.68 105.68 165.20 Cl− (aq) −167.16 −131.23 56.5 HCl(g) −92.31 −95.30 186.91 HCl(aq) −167.16 −131.23 56.5 Copper Cu(s) 0 0 33.15 Cu+(aq) 71.67 49.98 40.6 Cu2+(aq) 64.77 65.49 −99.6 Cu2O(aq) −168.6 −146.0 93.14 CuO(s) −157.3 −129.7 42.63 CuSO4(s) −771.36 −661.8 109 CuSO4.5H2O(s) −2279.7 −1879.7 300.4 (continued) Substance Enthalpy of formation, Gibbs Energy of formation, Entropy,* $\Delta f\ H^0$/ (kJ mol–1) $\Delta f\ G^0$/ (kJ mol–1) $S^0$/(J K–1 mol–1) ** For organic compounds, a separate table is provided in continuation. Rationalised 2023-24 222 chemistry Deuterium D2(g) 0 0 144.96 D2O(g) −249.20 −234.54 198.34 D2O(l) −294.60 −243.44 75.94 Fluorine F2(g) 0 0 202.78 F− (aq) −332.63 −278.79 −13.8 HF(g) −271.1 −273.2 173.78 HF(aq) −332.63 −278.79 −13.8 Hydrogen (see also Deuterium) H2(g) 0 0 130.68 H(g) 217.97 203.25 114.71 H+(aq) 0 0 0 H2O(l) −285.83 −237.13 69.91 H2O(g) −241.82 −228.57 188.83 H2O2(l) −187.78 −120.35

| Substance | $\Delta_f H^0$/ (kJ mol$^{-1}$) | $\Delta_f G^0$/ (kJ mol$^{-1}$) | $S^0$/(J K$^{-1}$ mol$^{-1}$) |
|---|---|---|---|
| | | | 109.6 |
| $H_2O_2$(aq) | –191.17 | –134.03 | 143.9 |
| **Iodine** | | | |
| $I_2$(s) | 0 | 0 | 116.14 |
| $I_2$(g) | 62.44 | 19.33 | 260.69 |
| $I^-$(aq) | –55.19 | –51.57 | 111.3 |
| HI(g) | 26.48 | 1.70 | 206.59 |
| **Iron** | | | |
| Fe(s) | 0 | 0 | 27.28 |
| $Fe^{2+}$(aq) | –89.1 | –78.90 | –137.7 |
| $Fe^{3+}$(aq) | –48.5 | –4.7 | –315.9 |
| $Fe_3O_4$(s), magnetite | –1118.4 | –1015.4 | 146.4 |
| $Fe_2O_3$(s), haematite | –824.2 | –742.2 | 87.40 |
| FeS(s,α) | –100.0 | –100.4 | 60.29 |
| FeS(aq) | — | 6.9 | — |
| $FeS_2$(s) | –178.2 | –166.9 | 52.93 |
| **Lead** | | | |
| Pb(s) | 0 | 0 | 64.81 |
| $Pb^{2+}$(aq) | –1.7 | –24.43 | 10.5 |
| $PbO_2$(s) | –277.4 | –217.33 | 68.6 |
| $PbSO_4$(s) | –919.94 | –813.14 | 148.57 |
| $PbBr_2$(s) | –278.7 | –261.92 | 161.5 |
| $PbBr_2$(aq) | –244.8 | –232.34 | 175.3 |
| **Magnesium** | | | |
| Mg(s) | 0 | 0 | 32.68 |
| Mg(g) | 147.70 | 113.10 | 148.65 |
| $Mg^{2+}$(aq) | –466.85 | –454.8 | –138.1 |
| MgO(s) | –601.70 | –569.43 | 26.94 |
| $MgCO_3$(s) | –1095.8 | –1012.1 | 65.7 |
| $MgBr_2$(s) | –524.3 | –503.8 | 117.2 |

(continued) Substance Enthalpy of formation, Gibbs Energy of formation, Entropy,* $\Delta_f H^0$/ (kJ mol$^{-1}$) $\Delta_f G^0$/ (kJ mol$^{-1}$) $S^0$/(J K$^{-1}$ mol$^{-1}$)

| Substance | $\Delta_f H^0$/ (kJ mol$^{-1}$) | $\Delta_f G^0$/ (kJ mol$^{-1}$) | $S^0$/(J K$^{-1}$ mol$^{-1}$) |
|---|---|---|---|
| **Mercury** | | | |
| Hg(1) | 0 | 0 | 76.02 |
| Hg(g) | 61.32 | 31.82 | 174.96 |
| HgO(s) | –90.83 | –58.54 | 70.29 |
| $Hg_2Cl_2$(s) | –265.22 | –210.75 | 192.5 |
| **Nitrogen** | | | |
| $N_2$(g) | 0 | 0 | 191.61 |
| NO(g) | 90.25 | 86.55 | 210.76 |
| $N_2O$(g) | 82.05 | 104.20 | 219.85 |
| $NO_2$(g) | 33.18 | 51.31 | 240.06 |
| $N_2O_4$(g) | 9.16 | 97.89 | 304.29 |
| $HNO_3$(1) | –174.10 | –80.71 | 155.60 |
| $HNO_3$(aq) | –207.36 | –111.25 | 146.4 |
| $NO_3^-$(aq) | –205.0 | –108.74 | 146.4 |
| $NH_3$(g) | –46.11 | –16.45 | 192.45 |
| $NH_3$(aq) | –80.29 | –26.50 | 111.3 |
| $NH_4^+$(aq) | –132.51 | –79.31 | 113.4 |
| $NH_2OH$(s) | –114.2 | — | — |
| $HN_3$(g) | 294.1 | 328.1 | 238.97 |
| $N_2H_4$(1) | 50.63 | 149.34 | 121.21 |
| $NH_4NO_3$(s) | –365.56 | –183.87 | 151.08 |
| $NH_4Cl$(s) | –314.43 | –202.87 | 94.6 |
| $NH_4ClO_4$(s) | –295.31 | –88.75 | 186.2 |
| **Oxygen** | | | |
| $O_2$(g) | 0 | 0 | 205.14 |
| $O_3$(g) | 142.7 | 163.2 | 238.93 |
| $OH^-$(aq) | –229.99 | –157.24 | –10.75 |
| **Phosphorus** | | | |
| P(s), white | 0 | 0 | 41.09 |
| $P_4$(g) | 58.91 | 24.44 | 279.98 |
| $PH_3$(g) | 5.4 | 13.4 | 210.23 |
| $P_4O_{10}$(s) | –2984.0 | –2697.0 | 228.86 |
| $H_3PO_3$(aq) | –964.8 | — | — |
| $H_3PO_4$(1) | –1266.9 | — | — |
| $H_3PO_4$(aq) | –1277.4 | –1018.7 | — |
| $PCl_3$(1) | –319.7 | –272.3 | 217.18 |
| $PCl_3$(g) | –287.0 | –267.8 | 311.78 |
| $PCl_5$(g) | –374.9 | –305.0 | 364.6 |
| **Potassium** | | | |
| K(s) | 0 | 0 | 64.18 |
| K(g) | 89.24 | 60.59 | 160.34 |
| $K^+$(aq) | –252.38 | –283.27 | 102.5 |
| KOH(s) | –424.76 | –379.08 | 78.9 |
| KOH(aq) | –482.37 | –440.50 | 91.6 |
| KF(s) | –567.27 | –537.75 | 66.57 |

(continued) Substance Enthalpy of formation, Gibbs Energy of formation, Entropy,* $\Delta_f H^0$/ (kJ mol$^{-1}$) $\Delta_f G^0$/ (kJ mol$^{-1}$) $S^0$/(J K$^{-1}$ mol$^{-1}$)

| Substance | $\Delta_f H^0$/ (kJ mol$^{-1}$) | $\Delta_f G^0$/ (kJ mol$^{-1}$) | $S^0$/(J K$^{-1}$ mol$^{-1}$) |
|---|---|---|---|
| **Potassium (continued)** | | | |
| KCl(s) | –436.75 | –409.14 | 82.59 |
| KBr(s) | –393.80 | –380.66 | 95.90 |
| KI(s) | –327.90 | –324.89 | 106.32 |
| $KClO_3$(s) | –397.73 | –296.25 | 143.1 |
| $KClO_4$(s) | –432.75 | –303.09 | 151.0 |
| $K_2S$(s) | –380.7 | –364.0 | 105 |
| $K_2S$(aq) | –471.5 | –480.7 | 190.4 |
| **Silicon** | | | |
| Si(s) | 0 | 0 | 18.83 |
| $SiO_2$(s,α) | –910.94 | –856.64 | 41.84 |
| **Silver** | | | |
| Ag(s) | 0 | 0 | 42.55 |
| $Ag^+$(aq) | 105.58 | 77.11 | 72.68 |
| $Ag_2O$(s) | –31.05 | –11.20 | 121.3 |
| AgBr(s) | –100.37 | –96.90 | 107.1 |
| AgBr(aq) | –15.98 | –26.86 | 155.2 |
| AgCl(s) | –127.07 | –109.79 | 96.2 |
| AgCl(aq) | –61.58 | –54.12 | 129.3 |
| AgI(s) | –61.84 | –66.19 | 115.5 |
| AgI(aq) | 50.38 | 25.52 | 184.1 |
| $AgNO_3$(s) | –124.39 | –33.41 | 140.92 |
| **Sodium** | | | |
| Na(s) | 0 | 0 | 51.21 |
| Na(g) | 107.32 | 76.76 | 153.71 |
| $Na^+$(aq) | –240.12 | –261.91 | 59.0 |
| NaOH(s) | –425.61 | –379.49 | 64.46 |
| NaOH(aq) | –470.11 | –419.15 | 48.1 |
| NaCl(s) | –411.15 | –384.14 | 72.13 |
| NaCl(aq) | –407.3 | –393.1 | 115.5 |
| NaBr(s) | –361.06 | –348.98 | 86.82 |
| NaI(s) | –287.78 | –286.06 | 98.53 |
| $NaHCO_3$(s) | –947.7 | –851.9 | 102.1 |
| $Na_2CO_3$(s) | –1130.9 | –1047.7 | 136.0 |
| **Sulphur** | | | |
| S(s), rhombic | 0 | 0 | 31.80 |
| S(s), monoclinic | 0.33 | 0.1 | 32.6 |
| $S^{2-}$(aq) | 33.1 | 85.8 | –14.6 |
| $SO_2$(g) | –296.83 | –300.19 | 248.22 |
| $SO_3$(g) | –395.72 | –371.06 | 256.76 |
| $H_2SO_4$(l) | –813.99 | –690.00 | 156.90 |
| $H_2SO_4$(aq) | –909.27 | –744.53 | 20.1 |
| $SO_4^{2-}$(aq) | –909.27 | –744.53 | 20.1 |
| $H_2S$(g) | –20.63 | –33.56 | 205.79 |
| $H_2S$(aq) | –39.7 | –27.83 | 121 |
| $SF_6$(g) | –1209 | –1105.3 | 291.82 |

Substance Enthalpy of formation, Gibbs Energy of formation, Entropy,* $\Delta_f H^0$/ (kJ mol$^{-1}$) $\Delta_f G^0$/ (kJ mol$^{-1}$) $S^0$/(J K$^{-1}$ mol$^{-1}$) (continued)

| Substance | $\Delta_f H^0$/ (kJ mol$^{-1}$) | $\Delta_f G^0$/ (kJ mol$^{-1}$) | $S^0$/(J K$^{-1}$ mol$^{-1}$) |
|---|---|---|---|
| **Tin** | | | |
| Sn(s), white | 0 | 0 | 51.55 |
| Sn(s), gray | –2.09 | 0.13 | 44.14 |
| SnO(s) | –285.8 | –256.9 | 56.5 |
| $SnO_2$(s) | –580.7 | –519.6 | 52.3 |
| **Zinc** | | | |
| Zn(s) | 0 | 0 | 41.63 |
| $Zn^{2+}$(aq) | –153.89 | –147.06 | –112.1 |
| ZnO(s) | –348.28 | –318.30 | 43.64 |
| Zn(g) | +130.73 | +95.14 | 160.93 |

*The entropies of individual ions in solution are determined by setting the entropy of $H^+$ in water equal to 0 and then defining the entropies of all other ions relative to this value; hence a negative entropy is one that is lower than the entropy of $H^+$ in water.

**ORGANIC COMPOUNDS**

| Substance | Enthalpy of combustion, $\Delta_c H^0$/ (kJ mol$^{-1}$) | Enthalpy of formation, $\Delta_f H^0$/ (kJ mol$^{-1}$) | Gibbs Energy of formation, $\Delta_f G^0$/ (kJ mol$^{-1}$) | Entropy, $S^0$/(J K$^{-1}$ mol$^{-1}$) |
|---|---|---|---|---|
| **Hydrocarbons** | | | | |
| $CH_4$(g), methane | –890 | –74.81 | –50.72 | 186.26 |
| $C_2H_2$(g), ethyne (acetylene) | –1300 | 226.73 | 209.20 | 200.94 |
| $C_2H_4$(g), ethene(ethylene) | –1411 | 52.26 | 68.15 | 219.56 |
| $C_2H_6$(g), ethane | –1560 | –84.68 | –32.82 | 229.60 |
| $C_3H_6$(g), propene (propylene) | –2058 | 20.42 | 62.78 | 266.6 |
| $C_3H_6$(g), cyclopropane | –2091 | 53.30 | 104.45 | 237.4 |
| $C_3H_8$(g), propane | –2220 | –103.85 | – | |

23.49 270.2 $C_4H_{10}(g)$, butane –2878 –126.15 –17.03 310.1 $C_5H_{12}(g)$, pentane –3537 –146.44 –8.20 349 $C_6H_6(l)$, benzene –3268 49.0 124.3 173.3 $C_6H_6(g)$ –3302 — — — $C_7H_8(l)$, toluene –3910 12.0 113.8 221.0 $C_7H_8(g)$ –3953 — — — $C_6H_{12}(l)$, cyclohexane –3920 –156.4 26.7 204.4 $C_6H_{12}(g)$, –3953 — — — $C_8H_{18}(l)$, octane –5471 –249.9 6.4 358 Alcohols and phenols $CH_3OH(l)$, methanol –726 –238.86 –166.27 126.8 $CH_3OH(g)$ –764 –200.66 –161.96 239.81 $C_2H_5OH(l)$, ethanol –1368 –277.69 –174.78 160.7 $C_2H_5OH(g)$ –1409 –235.10 –168.49 282.70 $C_6H_5OH(s)$, phenol –3054 –164.6 –50.42 144.0 (continued) Substance Enthalpy of formation, Gibbs Energy of formation, Entropy,* $\Delta_f H^0$/ (kJ mol–1) $\Delta_f G^0$/ (kJ mol–1) $S^0$/(J K–1 mol–1) Rationalised 2023-24 226 chemistry Carboxylic acid $HCOOH(l)$, formic acid –255 –424.72 –361.35 128.95 $CH_3COOH(l)$, acetic acid –875 –484.5 –389.9 159.8 $CH_3COOH (aq)$ — –485.76 –396.64 86.6 $(COOH)_2(s)$, oxalic acid –254 –827.2 –697.9 120 $C_6H_5COOH(s)$, benzoic acid –3227 –385.1 –245.3 167.6 Aldehydes and ketones $HCHO(g)$, methanal –571 –108.57 –102.53 218.77 (formaldehyde) $CH_3CHO(l)$, ethanal –1166 –192.30 –128.12 160.2 (acetaldehyde) $CH_3CHO(g)$ –1192 –166.19 –128.86 250.3 $CH_3COCH_3(l)$, propanone –1790 –248.1 –155.4 200 (acetone) Sugars $C_6H_{12}O_6(s)$, glucose –2808 –1268 –910 212 $C_6H_{12}O_6(aq)$ — — –917 — $C_6H_{12}O_6(s)$, fructose –2810 –1266 — — $C_{12}H_{22}O_{11}(s)$, sucrose –5645 –2222 –1545 360 Nitrogen compounds $CO(NH_2)_2(s)$, urea –632 –333.51 –197.33 104.60 $C_6H_5NH_2(l)$, aniline –3393 31.6 149.1 191.3 $NH_2CH_2COOH(s)$, glycine –969 –532.9 –373.4 103.51 $CH_3NH_2(g)$, methylamine –1085 –22.97 32.16 243.41 Substance Enthalpy of Enthalpy of Gibbs Energy of combustion, formation, formation, Entropy, $\Delta_c H^0$/ (kJ mol–1) $\Delta_f H^0$/ (kJ mol–1) $\Delta_f G^0$/ (kJ mol–1) $S^0$/(J K–1 mol–1) Rationalised 2023-24 Appendices 227 Standard potentials at 298 K in electrochemical order Reduction half-reaction $E^0$/V $H_4XeO_6 + 2H^+ + 2e^- \rightarrow XeO_3 + 3H_2O$ +3.0 $F_2 + 2e^- \rightarrow 2F^-$ +2.87 $O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O$ +2.07 $S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}$ +2.05 $Ag^+ + e^- \rightarrow Ag^+$ +1.98 $Co^{3+} + e^- \rightarrow Co^{2+}$ +1.81 $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ +1.78 $Au^+ + e^- \rightarrow Au$ +1.69 $Pb^{4+} + 2e^- \rightarrow Pb^{2+}$ +1.67 $2HClO + 2H^+ + 2e^- \rightarrow Cl_2 + 2H_2O$ +1.63 $Ce^{4+} + e^- \rightarrow Ce^{3+}$ +1.61 $2HBrO + 2H^+ + 2e^- \rightarrow Br_2 + 2H_2O$ +1.60 $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ +1.51 $Mn^{3+} + e^- \rightarrow Mn^{2+}$ +1.51 $Au^{3+} + 3e^- \rightarrow Au$ +1.40 $Cl_2 + 2e^- \rightarrow 2Cl^-$ +1.36 $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ +1.33 $O_3 + H_2O + 2e^- \rightarrow O_2 + 2OH^-$ +1.24 $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ +1.23 $ClO_4^- + 2H^+ +2e^- \rightarrow ClO_3^- + 2H_2O$ +1.23 $MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$ +1.23 $Pt^{2+} + 2e^- \rightarrow Pt$ +1.20 $Br_2 + 2e^- \rightarrow 2Br^-$ +1.09 $Pu^{4+} + e^- \rightarrow Pu^{3+}$ +0.97 $NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$ +0.96 $2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$ +0.92 $ClO^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^-$ +0.89 $Hg^{2+} + 2e^- \rightarrow Hg$ +0.86 $NO_3^- + 2H^+ + e^- \rightarrow NO_2 + H_2O$ +0.80 $Ag^+ + e^- \rightarrow Ag$ +0.80 $Hg_2^{2+} +2e^- \rightarrow 2Hg$ +0.79 $Fe^{3+} + e^- \rightarrow Fe^{2+}$ +0.77 $BrO^- + H_2O + 2e^- \rightarrow Br^- + 2OH^-$ +0.76 $Hg_2SO_4 +2e^- \rightarrow 2Hg + SO_4^{2-}$ +0.62 $MnO_4^{2-} + 2H_2O + 2e^- \rightarrow MnO_2 + 4OH^-$ +0.60 $MnO_4^- + e^- \rightarrow MnO_4^{2-}$ +0.56 $I_2 + 2e^- \rightarrow 2I^-$ +0.54 $I_3^- + 2e^- \rightarrow 3I^-$ +0.53 Reduction half-reaction $E^0$/V $Cu^+ + e^- \rightarrow Cu$ +0.52 $NiOOH + H_2O + e^- \rightarrow Ni(OH)_2 + OH^-$ +0.49 $Ag_2CrO_4 + 2e^- \rightarrow 2Ag + CrO_4^{2-}$ +0.45 $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ +0.40 $ClO_4^- + H_2O + 2e^- \rightarrow ClO_3^- + 2OH^-$ +0.36 $[Fe(CN)_6]^{3-} + e^- \rightarrow [Fe(CN)_6]^{4-}$ +0.36 $Cu^{2+} + 2e^- \rightarrow Cu$ +0.34 $Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$ +0.27 $AgCl + e^- \rightarrow Ag + Cl^-$ +0.27 $Bi^{3+} + 3e^- \rightarrow Bi$ +0.20 $SO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SO_3 + H_2O$ +0.17 $Cu^{2+} + e^- \rightarrow Cu^+$ +0.16 $Sn^{4+} + 2e^- \rightarrow Sn^{2+}$ +0.15 $AgBr + e^- \rightarrow Ag + Br^-$ +0.07 $Ti^{4+} + e^- \rightarrow Ti^{3+}$ 0.00 $2H^+ + 2e^- \rightarrow H_2$ 0.0 by definition $Fe^{3+} + 3e^- \rightarrow Fe$ –0.04 $O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^-$ –0.08 $Pb^{2+} + 2e^- \rightarrow Pb$ –0.13 $In^+ + e^- \rightarrow In$ –0.14 $Sn^{2+} + 2e^- \rightarrow Sn$ –0.14 $AgI + e^- \rightarrow Ag + I^-$ –0.15 $Ni^{2+} + 2e^- \rightarrow Ni$ –0.23 $V^{3+} + e^- \rightarrow V^{2+}$ –0.26 $Co^{2+} + 2e^- \rightarrow Co$ –0.28 $In^{3+} + 3e^- \rightarrow In$ –0.34 $Tl^+ + e^- \rightarrow Tl$ –0.34 $PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$ –0.36 $Ti^{3+} + e^- \rightarrow Ti^{2+}$ –0.37 $Cd^{2+} + 2e^- \rightarrow Cd$ –0.40 $In^{2+} + e^- \rightarrow In^+$ –0.40 $Cr^{3+} + e^- \rightarrow Cr^{2+}$ –0.41 $Fe^{2+} + 2e^- \rightarrow Fe$ –0.44 $In^{3+} + 2e^- \rightarrow In^+$ –0.44 $S + 2e^- \rightarrow S^{2-}$ –0.48 $In^{3+} + e^- \rightarrow In^{2+}$ –0.49 $U^{4+} + e^- \rightarrow U^{3+}$ –0.61 $Cr^{3+} + 3e^- \rightarrow Cr$ –0.74 $Zn^{2+} + 2e^- \rightarrow Zn$ –0.76 (continued) Appendix VII Rationalised 2023-24 228 chemistry Reduction half-reaction $E^0$/V $Cd(OH)_2 + 2e^- \rightarrow Cd + 2OH^-$ –0.81 $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ –0.83 $Cr^{2+} + 2e^- \rightarrow Cr$ –0.91 $Mn^{2+} + 2e^- \rightarrow Mn$ –1.18 $V^{2+} + 2e^- \rightarrow V$ –1.19 $Ti^{2+} + 2e^- \rightarrow Ti$ –1.63 $Al^{3+} + 3e^- \rightarrow Al$ –1.66 $U^{3+} + 3e^-$

→ U –1.79 Sc3+ + 3e– → Sc –2.09 Mg2+ + 2e– → Mg –2.36 Ce3+ + 3e– → Ce –2.48 Reduction half-reaction E0/V La3+ + 3e– → La –2.52 Na+ + e– → Na –2.71 Ca2+ + 2e– → Ca –2.87 Sr2+ + 2e– → Sr –2.89 Ba2+ + 2e– → Ba –2.91 Ra2+ + 2e– → Ra –2.92 Cs+ + e– → Cs –2.92 Rb+ + e– → Rb –2.93 K+ +e– → K –2.93 Li+ + e– → Li –3.05 Appendix continued Rationalised 2023-24answers 229 Unit 1 1.17 ~ 15 × 10–4 g , 1.25 × 10–4 m 1.18 (i) 4.8 × 10–3 (ii) 2.34 × 105 (iii) 8.008 × 103 (iv) 5.000 × 102 (v) 6.0012 1.19 (i) 2 (ii) 3 (iii) 4 (iv) 3 (v) 4 (vi) 5 1.20 (i) 34.2 (ii) 10.4 (iii) 0.0460 (iv) 2810 1.21 (a) law of multiple proportion (b) (i) Ans : (106 mm, 1015 pm) (ii) Ans : (10–6 kg, 106 ng) (iii) Ans : (10–3 L, 10–3 dm3 ) 1.22 6.00 × 10–1 m =0.600 m 1.23 (i) B is limiting (ii) A is limiting (iii) Stoichiometric mixture –No (iv) B is limiting (v) A is limiting 1.24 (i) 2.43 × 103 g (ii) Yes (iii) Hydrogen will remain unreacted; 5.72 × 102 g 1.26 Ten volumes 1.27 (i) 2.87 × 10–11m (ii) 1.515 × 10–11 m (iii) 2.5365 × 10–2kg 1.30 1.99265 × 10–23g 1.31 (i) 3 (ii) 4 (iii) 4 1.32 39.948 g mol–1 1.33 (i) 3.131 × 1025 atoms (ii) 13 atoms (iii) 7.8286 × 1024 atoms 1.34 Empirical formula CH, molar mass 26.0 g mol–1, molecular formula C2H2 1.35 0.94 g CaCO3 1.36 8.40 g HCl UNIT 2 2.1 (i) 1.099 × 1027 electrons (ii) 5.48 × 10–7 kg, 9.65 × 104 C 2.2 (i) 6.022 × 1024 electrons (ii) (a) 2.4088 × 1021 neutrons (b) 4.0347 × 10–6 kg (iii) (a) 1.2044 × 1022 protons (b) 2.015 × 10–5 kg 2.3 7,6: 8,8: 12,12: 30,26: 50, 38 2.4 (i) Cl (ii) U (iii) Be 2.5 5.17 × 1014 s–1, 1.72 × 106 m–1 2.6 (i) 1.988 × 10–18 J (ii) 3.98 × 10–15 J Answer to Some Selected Problems Rationalised 2023-24 230 chemistry 2.7 6.0 × 10–2 m, 5.0 × 109 s–1 and 16.66 m–1 2.8 2.012 × 1016 photons 2.9 (i) 4.97 × 10–19 J (3.10 eV); (ii) 0.97 eV (iii) 5.84 × 105 m s–1 2.10 494 kJ mol–1 2.11 7.18 × 1019s–1 2.12 4.41 × 1014s–1, 2.91 × 10–19J 2.13 486 nm 2.14 8.72 × 10–20J 2.15 15 emission lines 2.16 (i) 8.72 × 10–20J (ii) 1.3225 nm 2.17 1.523 × 106 m–1 2.18 2.08 × 10–11 ergs, 950 Å 2.19 3647Å 2.20 3.55 × 10–11m 2.21 8967Å 2.22 Na+ , Mg2+, Ca2+; Ar, S2– and K+ 2.23 (i) (a) 1s2 (b) 1s2 2s2 2p6 ; (c) 1s2 2s2 2p6 (d) 1s2 2s2 2p6 2.24 n = 5 2.25 n = 3; l = 2; ml = –2, –1, 0, +1, +2 (any one value) 2.26 (i) 29 protons 2.27 1, 2, 15 2.28 (i) l ml 0 0 1 – 1,0,+1 2 –2,–1,0,+1,+2 (ii) l = 2; ml =–2, –1,0,+1,+2 (iii) 2s, 2p 2.29 (a) 1s, (b) 3p, (c) 4d and (d) 4f 2.30 (a), (c) and (e) are not possible 2.31 (a) 16 electrons (b) 2 electrons 2.33 n = 2 to n = 1 2.34 8.72 × 10–18J per atom 2.35 1.33 × 109 2.36 0.06 nm 2.37 (a) 1.3 × 102 pm (b) 6.15 × 107 pm 2.38 1560 2.39 8 2.40 More number of K–particles will pass as the nucleus of the lighter atoms is small, smaller number of K–particles will be deflected as a number of positve charges is less than on the lighter nuclei. 2.41 For a given element the number of prontons is the same for the isotopes, whereas the mass number can be different for the given atomic number. 2.42 35 81Br 2.43 17 37 1 Cl– Rationalised 2023-24 answers 231 2.44 26 56 3+ Fe 2.45 Cosmic rays > X–rays > amber colour > microwave > FM 2.46 3.3 × 106 J 2.47 (a) 4.87 × 1014 s–1 (b) 9.0 × 109 m (c) 32.27 × 10–20 J (d) 6.2 × 1018 quanta 2.48 10 2.49 8.28 × 10–10 J 2.50 3.45 × 10–22 J 2.51 (a) Threshold wave length (b) Threshold frequency of radiation 652.46 nm 4.598 ×1014 s–1 (c) Kinetic energy of ejected photoelectron 9.29 ×10–20 J, Velocity of photoelectron 4.516 × 105 ms–1 2.52 530.9nm 2.53 4.48 eV 2.54 7.6 × 103 eV 2.55 infrared, 5 2.56 434 nm 2.57 455 pm 2.58 494.5 ms–1 2.59 332 pm 2.60 1.516 × 10–38 m 2.61 Cannot be defined as the actual magnitude is smaller than uncertainty. 2.62 (v) < (ii) = (iv) < (vi) = (iii) < (i) 2.63 4p 2.64 (i) 2s (ii) 4d (iii) 3p 2.65 Si 2.66 (a) 3 (b) 2 (c) 6 (d) 4 (e) zero 2.67 16 UNIT 5 5.1 (ii) 5.2 (iii) 5.3 (ii) 5.4 (iii) 5.5 (i) 5.6 (iv) 5.7 q = + 701 J w = – 394 J, since work is done by the system ΔU = 307 J 5.8 –743.939 kJ 5.9 1.067 kJ 5.10 ΔH = –7.151 kJ mol–1 Rationalised 2023-24 232 chemistry 5.11 – 314.8 kJ 5.12 ΔrH = –778 kJ 5.13 – 46.2 kJ mol–1 5.14 – 239 kJ mol–1 5.15 326 kJ mol–1 5.16 ΔS > 0 5.17 2000 K 5.18 ΔH is negative (bond energy is released) and ΔS is negative (There is less randomness among the molecules than among the atoms) 5.19 0.164 kJ, the reaction is not spontaneous. 5.20 –5.744 kJ mol–1 5.21 NO(g) is unstable, but NO2(g) is formed. 5.22 qsurr = + 286 kJ mol–1 ΔSsurr = 959.73 J K–1 UNIT 6 6.2 12.229 6.3 2.67 × 104 6.5 (i) 4.33 × 10–4 (ii) 1.90 6.6 1.59 × 10–15 6.8 [N2] = 0.0482 molL–1, [O2] = 0.0933 molL–1, [N2O] = 6.6 × 10–21 molL–1 6.9 0.0352mol of NO and 0.0178mol of Br2 6.10 7.47 × 1011 M–1 6.11 4.0 6.12 Qc = 2.379 × 103 . No, reaction is not at equilibrium. 6.14 0.44 6.15 0.068 molL–1 each of H2 and I2 6.16 [I2] = [Cl2] = 0.167

M, [ICl] = 0.446 M 6.17 $[C_2H_6]_{eq}$ = 3.62 atm 6.18 (i) $[CH_3COOC_2H_5][H_2O]$ / $[CH_3COOH][C_2H_5OH]$ (ii) 3.92 (iii) value of $Q_c$ is less than $K_c$ therefore equilibrium is not attained. 6.19 0.02molL–1 for both. 6.20 [PCO] = 1.739atm, [PCO2] = 0.461atm. 6.21 No, the reaction proceeds to form more products. 6.22 3 × 10–4 molL–1 6.23 0.149 6.24 a) – 35.0kJ, b) 1.365 × 106 6.27 $[PH_2]_{eq}$ = $[PBr_2]_{eq}$ = 2.5 × 10–2bar, [PHBr] = 10.0 bar 6.30 b) 120.48 6.31 $[H_2]_{eq}$ = 0.96 bar 6.33 2.86 × 10–28 M 6.34 5.85x10–2 6.35 $NO_2^-$ , HCN, $ClO_4$, HF, $H_2O$, $HCO_3^-$ , $HS^-$ 6.36 $BF_3$, $H^+$ , $NH_4^+$ Rationalised 2023-24 answers 233 6.37 $F^-$ , $HSO_4^-$ , $CO_3^{2-}$ 6.38 $NH_3$, $NH_4^+$ , HCOOH 6.41 2.42 6.42 1.7 x 10–4M 6.43 $F^-$ = 1.5 x 10–11, $HCOO^-$ = 5.6 × 10–11, $CN^-$ = 2.08 x 10–6 6.44 [phenolate ion]= 2.2 × 10–6, α = 4.47 × 10–5 , α in sodium phenolate = 10–8 6.45 $[HS^-]$ = 9.54 x 10–5, in 0.1M HCl $[HS^-]$ = 9.1 × 10–8M, $[S^{2-}]$ = 1.2 × 10–13M, in 0.1M HCl $[S^{2-}]$= 1.09 × 10–19M 6.46 $[Ac^-]$ = 0.00093, pH= 3.03 6.47 $[A^-]$ = 7.08 x10–5M, $K_a$= 5.08 × 10–7, $pK_a$= 6.29 6.48 a) 2.52 b) 11.70 c) 2.70 d) 11.30 6.49 a) 11.65 b) 12.21 c) 12.57 c) 1.87 6.50 pH = 1.88, $pK_a$ = 2.70 6.51 $K_b$ = 1.6 × 10–6, $pK_b$ = 5.8 6.52 α = 6.53 × 10–4, $K_a$ = 2.35 × 10–5 6.53 a) 0.0018 b) 0.00018 6.54 α = 0.0054 6.55 a) 1.48 × 10–7M, b) 0.063 c) 4.17 × 10–8M d) 3.98 × 10–7 6.56 a) 1.5 × 10–7M, b) 10–5M, c) 6.31 × 10–5M d) 6.31 × 10–3M 6.57 $[K^+]$ = $[OH^-]$ = 0.05M, $[H^+]$ = 2.0 × 10–13M 6.58 $[Sr^{2+}]$ = 0.1581M, $[OH^-]$ = 0.3162M, pH = 13.50 6.59 α = 1.63 × 10–2, pH = 3.09. In presence of 0.01M HCl, α = 1.32 × 10–3 6.60 $K_a$ = 2.09 × 10–4 and degree of ionization = 0.0457 6.61 pH = 7.97. Degree of hydrolysis = 2.36 × 10–5 6.62 $K_b$ = 1.5 × 10–9 6.63 NaCl, KBr solutions are neutral, NaCN, NaNO2 and KF solutions are basic and NH4NO3 solution is acidic. 6.64 (a) pH of acid solution= 1.9 (b) pH of its salt solution= 7.9 6.65 pH = 6.78 6.66 a) 12.6 b) 7.00 c) 1.3 6.67 Silver chromate S= 0.65 × 10–4M; Molarity of $Ag^+$ = 1.30 x 10–4M Molarity of $CrO_4^{2-}$ = 0.65 × 10–4M; Barium Chromate S = 1.1 × 10–5M; Molarity of $Ba^{2+}$ and $CrO_4^{2-}$ each is 1.1 × 10–5M; Ferric Hydroxide S = 1.39 × 10–10M; Molarity of $Fe^{3+}$ = 1.39 × 10–10M; Molarity of $[OH^-]$ = 4.17 × 10–10M Lead Chloride S = 1.59 × 10–2M; Molarity of $Pb^{2+}$ = 1.59 × 10–2M Molarity of $Cl^-$ = 3.18 × 10–2M; Mercurous Iodide S = 2.24 × 10–10M; Molarity of $Hg_2^{2+}$ = 2.24 × 10–10M and molarity of $I^-$ = 4.48 × 10–10M 6.68 Silver chromate is more soluble and the ratio of their molarities = 91.9 6.69 No precipitate 6.70 Silver benzoate is 3.317 times more soluble at lower pH 6.71 The highest molarity for the solution is 2.5 × 10–9M 6.72 2.43 litre of water 6.73 Precipitation will take place in cadmium chloride solution Rationalised 2023-24 Notes Rationalised 2023-24Chemistry Part I Textbook for Class XI Rationalised 2023-24

Rationalised 2023-24 answerS 3 Foreword The National Curriculum Framework (NCF), 2005 recommends that children's life at school must be linked to their life outside the school. This principle marks a departure from the legacy of bookish learning which continues to shape our system and causes a gap between the school, home and community. The syllabi and textbooks developed on the basis of NCF signify an attempt to implement this basic idea. They also attempt to discourage rote learning and the maintenance of sharp boundaries between different subject areas. We hope these measures will take us significantly further in the direction of a child-centred system of education outlined in the National Policy on Education (1986). The success of this effort depends on the steps that school principals and teachers will take to encourage children to reflect on their own learning and to pursue imaginative activities and questions. We must recognise that, given space, time and freedom, children generate new knowledge by engaging with the information passed on to them by adults. Treating the prescribed textbook as the sole basis of examination is one of the key reasons why other resources and sites of learning are ignored. Inculcating creativity and initiative is possible if we perceive and treat children as participants in learning, not as receivers of a fixed body of knowledge. These aims imply considerable change in school routines and mode of functioning. Flexibility in the daily time-table is as necessary as rigour in implementing the annual calender so that the required number of teaching days are actually devoted to teaching. The methods used for teaching and evaluation will also determine how effective this textbook proves for making children's life at school a happy experience, rather than a source of stress or boredom. Syllabus designers have tried to address the problem of curricular burden by restructuring and reorienting knowledge at different stages with greater consideration for child psychology and the time available for teaching. The textbook attempts to enhance this endeavour by giving higher priority and space to opportunities for contemplation and wondering, discussion in small groups, and activities requiring hands-on experience. The National Council of Educational Research and Training (NCERT) appreciates the hard work done by the textbook development committee responsible for this book. We wish to thank the Chairperson of the advisory group in science and mathematics, Professor J.V. Narlikar and the Chief Advisor for this book, Professor B. L. Khandelwal for guiding the work of this committee. Several teachers contributed to the development of this textbook; we are grateful to their principals for making this possible. We are indebted to the institutions and organisations which have generously permitted us to draw upon their resources, material and personnel. As an organisation committed to systemic reform and continuous improvement in the quality of its products, NCERT welcomes comments and suggestions which will enable us to undertake further revision and refinement. Director New Delhi National Council of Educational 20 December 2005 Research and Training Rationalised 2023-24 4 chemistry Rationalised 2023-24 answerS 5 Rationalisation of Content in the Textbooks In view of the COVID-19 pandemic, it is imperative to reduce content load on students. The National Education Policy 2020, also emphasises reducing the content load and providing opportunities for experiential learning with creative mindset. In this background, the NCERT has undertaken the exercise to rationalise the textbooks across all classes. Learning Outcomes already developed by the NCERT across classes have been taken into consideration in this exercise. Contents of the textbooks have been rationalised in view of the following: • Overlapping with similar content included in other subject areas in the same class • Similar content included in the lower or higher class in the same subject • Difficulty level • Content, which is easily accessible to students

without much interventions from teachers and can be learned by children through self-learning or peer-learning • Content, which is irrelevant in the present context This present edition, is a reformatted version after carrying out the changes given above.

# Contents

# Unit 1 Some Basic Concepts of Chemistry

Science can be viewed as a continuing human effort to systematise knowledge for describing and understanding nature. You have learnt in your previous classes that we come across diverse substances present in nature and changes in them in daily life. Curd formation from milk, formation of vinegar from sugarcane juice on keeping for prolonged time and rusting of iron are some of the examples of changes which we come across many times. For the sake of convenience, science is sub-divided into various disciplines: chemistry, physics, biology, geology, etc. The branch of science that studies the preparation, properties, structure and reactions of material substances is called chemistry. Development of chemistry Chemistry, as we understand it today, is not a very old discipline. Chemistry was not studied for its own sake, rather it came up as a result of search for two interesting things: i. Philosopher's stone (Paras) which would convert all baser metals e.g., iron and copper into gold. ii. 'Elixir of life' which would grant immortality. People in ancient India, already had the knowledge of many scientific phenomenon much before the advent of modern science. They applied that knowledge in various walks of life. Chemistry developed mainly in the form of Alchemy and Iatrochemistry during 1300-1600 CE. Modern chemistry took shape in the 18th century Europe, after a few centuries of alchemical traditions which were introduced in Europe by the Arabs. After studying this unit, you will be able to • appreciate the contribution of India in the development of chemistry understand the role of chemistry in different spheres of life; • explain the characteristics of three states of matter; • classify different substances into elements, compounds and mixtures; • use scientific notations and determine significant figures; • differentiate between precision and accuracy; • define SI base units and convert physical quantities from one system of units to another; • explain various laws of chemical combination; • appreciate significance of atomic mass, average atomic

mass, molecular mass and formula mass; • describe the terms – mole and molar mass; • calculate the mass per cent of component elements constituting a compound; • determine empirical formula and molecular formula for a compound from the given experimental data; and • perform the stoichiometric calculations. Chemistry is the science of molecules and their transformations. It is the science not so much of the one hundred elements but of the infinite variety of molecules that may be built from them. Roald Hoffmann Rationalised 2023-24 2 chemistry Other cultures – especially the Chinese and the Indian – had their own alchemical traditions. These included much knowledge of chemical processes and techniques. In ancient India, chemistry was called Rasayan Shastra, Rastantra, Ras Kriya or Rasvidya. It included metallurgy, medicine, manufacture of cosmetics, glass, dyes, etc. Systematic excavations at Mohenjodaro in Sindh and Harappa in Punjab prove that the story of development of chemistry in India is very old. Archaeological findings show that baked bricks were used in construction work. It shows the mass production of pottery, which can be regarded as the earliest chemical process, in which materials were mixed, moulded and subjected to heat by using fire to achieve desirable qualities. Remains of glazed pottery have been found in Mohenjodaro. Gypsum cement has been used in the construction work. It contains lime, sand and traces of $CaCO_3$. Harappans made faience, a sort of glass which was used in ornaments. They melted and forged a variety of objects from metals, such as lead, silver, gold and copper. They improved the hardness of copper for making artefacts by using tin and arsenic. A number of glass objects were found in Maski in South India (1000–900 BCE), and Hastinapur and Taxila in North India (1000–200 BCE). Glass and glazes were coloured by addition of colouring agents like metal oxides. Copper metallurgy in India dates back to the beginning of chalcolithic cultures in the subcontinent. There are much archeological evidences to support the view that technologies for extraction of copper and iron were developed indigenously. According to Rigveda, tanning of leather and dying of cotton were practised during 1000–400 BCE. The golden gloss of the black polished ware of northen India could not be replicated and is still a chemical mystery. These wares indicate the mastery with which kiln temperatures could be controlled. Kautilya's Arthashastra describes the production of salt from sea. A vast number of statements and material described in the ancient Vedic literature can be shown to agree with modern scientific findings. Copper utensils, iron, gold, silver ornaments and terracotta discs and painted grey pottery have been found in many archaeological sites in north India. Sushruta Samhita explains the importance of Alkalies. The Charaka Samhita mentions ancient indians who knew how to prepare sulphuric acid, nitric acid and oxides of copper, tin and zinc; the sulphates of copper, zinc and iron and the carbonates of lead and iron. Rasopanishada describes the preparation of gunpowder mixture. Tamil texts also describe the preparation of fireworks using sulphur, charcoal, saltpetre (i.e., potassium nitrate), mercury, camphor, etc. Nagarjuna was a great Indian scientist. He was a reputed chemist, an alchemist and a metallurgist. His work Rasratnakar deals with the formulation of mercury compounds. He has also discussed methods for the extraction of metals, like gold, silver, tin and copper. A book, Rsarnavam, appeared around 800 CE. It discusses the uses of various furnaces, ovens and crucibles for different purposes. It describes methods by which metals could be identified by flame colour. Chakrapani discovered mercury sulphide. The credit for inventing soap also goes to him. He used mustard oil and some alkalies as ingredients for making soap. Indians began making soaps in the 18th century CE. Oil of Eranda and seeds of Mahua plant and calcium carbonate were used for making soap. The paintings found on the walls of Ajanta and Ellora, which look fresh even after ages, testify to a high level of science achieved in ancient India. Varähmihir's Brihat Samhita is a sort of encyclopaedia, which was composed in the sixth century CE. It informs about the preparation of glutinous material to be applied on walls and roofs of houses and temples. It was prepared entirely from extracts of various plants, fruits, seeds and barks, which were concentrated by boiling, and then, treated with various resins. It will be interesting to test such materials scientifically and assess them for use. Rationalised 2023-24 Some Basic Concepts of

Chemistry 3 A number of classical texts, like Atharvaveda (1000 BCE) mention some dye stuff, the material used were turmeric, madder, sunflower, orpiment, cochineal and lac. Some other substances having tinting property were kamplcica, pattanga and jatuka. Varähmihir's Brihat Samhita gives references to perfumes and cosmetics. Recipes for hair dying were made from plants, like indigo and minerals like iron power, black iron or steel and acidic extracts of sour rice gruel. Gandhayukli describes recipes for making scents, mouth perfumes, bath powders, incense and talcum power. Paper was known to India in the 17th century as account of Chinese traveller I-tsing describes. Excavations at Taxila indicate that ink was used in India from the fourth century. Colours of ink were made from chalk, red lead and minimum. It seems that the process of fermentation was well-known to Indians. Vedas and Kautilya's Arthashastra mention about many types of liquors. Charaka Samhita also mentions ingredients, such as barks of plants, stem, flowers, leaves, woods, cereals, fruits and sugarcane for making Asavas. The concept that matter is ultimately made of indivisible building blocks, appeared in India a few centuries BCE as a part of philosophical speculations. Acharya Kanda, born in 600 BCE, originally known by the name Kashyap, was the first proponent of the 'atomic theory'. He formulated the theory of very small indivisible particles, which he named 'Paramãnu' (comparable to atoms). He authored the text Vaiseshika Sutras. According to him, all substances are aggregated form of smaller units called atoms (Paramãnu), which are eternal, indestructible, spherical, suprasensible and in motion in the original state. He explained that this individual entity cannot be sensed through any human organ. Kanda added that there are varieties of atoms that are as different as the different classes of substances. He said these (Paramãnu) could form pairs or triplets, among other combinations and unseen forces cause interaction between them. He conceptualised this theory around 2500 years before John Dalton (1766-1844). Charaka Samhita is the oldest Ayurvedic epic of India. It describes the treatment of diseases. The concept of reduction of particle size of metals is clearly discussed in Charaka Samhita. Extreme reduction of particle size is termed as nanotechnology. Charaka Samhita describes the use of bhasma of metals in the treatment of ailments. Now-a-days, it has been proved that bhasmas have nanoparticles of metals. After the decline of alchemy, Iatrochemistry reached a steady state, but it too declined due to the introduction and practise of western medicinal system in the 20th century. During this period of stagnation, pharmaceutical industry based on Ayurveda continued to exist, but it too declined gradually. It took about 100-150 years for Indians to learn and adopt new techniques. During this time, foreign products poured in. As a result, indigenous traditional techniques gradually declined. Modern science appeared in Indian scene in the later part of the nineteenth century. By the mid-nineteenth century, European scientists started coming to India and modern chemistry started growing. From the above discussion, you have learnt that chemistry deals with the composition, structure, properties and interection of matter and is of much use to human beings in daily life. These aspects can be best described and understood in terms of basic constituents of matter that are atoms and molecules. That is why, chemistry is also called the science of atoms and molecules. Can we see, weigh and perceive these entities (atoms and molecules)? Is it possible to count the number of atoms and molecules in a given mass of matter and have a quantitative relationship between the mass and the number of these particles? We will get the answer of some of these questions in this Unit. We will further describe how physical properties of matter can be quantitatively described using numerical values with suitable units. Rationalised 2023-24 4 chemistry 1.1 IMPORTANCE OF CHEMISTRY Chemistry plays a central role in science and is often intertwined with other branches of science. Principles of chemistry are applicable in diverse areas, such as weather patterns, functioning of brain and operation of a computer, production in chemical industries, manufacturing fertilisers, alkalis, acids, salts, dyes, polymers, drugs, soaps, detergents, metals, alloys, etc., including new material. Chemistry contributes in a big way to the national economy. It also plays an important role in meeting human needs for food, healthcare products and other material aimed at improving the

quality of life. This is exemplified by the large-scale production of a variety of fertilisers, improved variety of pesticides and insecticides. Chemistry provides methods for the isolation of lifesaving drugs from natural sources and makes possible synthesis of such drugs. Some of these drugs are cisplatin and taxol, which are effective in cancer therapy. The drug AZT (Azidothymidine) is used for helping AIDS patients. Chemistry contributes to a large extent in the development and growth of a nation. With a better understanding of chemical principles it has now become possible to design and synthesise new material having specific magnetic, electric and optical properties. This has lead to the production of superconducting ceramics, conducting polymers, optical fibres, etc. Chemistry has helped in establishing industries which manufacture utility goods, like acids, alkalies, dyes, polymesr metals, etc. These industries contribute in a big way to the economy of a nation and generate employment. In recent years, chemistry has helped in dealing with some of the pressing aspects of environmental degradation with a fair degree of success. Safer alternatives to environmentally hazardous refrigerants, like CFCs (chlorofluorocarbons), responsible for ozone depletion in the stratosphere, have been successfully synthesised. However, many big environmental problems continue to be matters of grave concern to the chemists. One such problem is the management of the Green House gases, like methane, carbon dioxide, etc. Understanding of biochemical processes, use of enzymes for large-scale production of chemicals and synthesis of new exotic material are some of the intellectual challenges for the future generation of chemists. A developing country, like India, needs talented and creative chemists for accepting such challenges. To be a good chemist and to accept such challanges, one needs to understand the basic concepts of chemistry, which begin with the concept of matter. Let us start with the nature of matter. 1.2 Nature of Matter You are already familiar with the term matter from your earlier classes. Anything which has mass and occupies space is called matter. Everything around us, for example, book, pen, pencil, water, air, all living beings, etc., are composed of matter. You know that they have mass and they occupy space. Let us recall the characteristics of the states of matter, which you learnt in your previous classes. 1.2.1 States of Matter You are aware that matter can exist in three physical states viz. solid, liquid and gas. The constituent particles of matter in these three states can be represented as shown in Fig. 1.1. Particles are held very close to each other in solids in an orderly fashion and there is not much freedom of movement. In liquids, the particles are close to each other but they can move around. However, in gases, the particles are far apart as compared to those present in solid or liquid states and their movement is easy and fast. Because of such arrangement of particles, different states of matter exhibit the following characteristics: (i) Solids have definite volume and definite shape. (ii) Liquids have definite volume but do not have definite shape. They take the shape of the container in which they are placed. Rationalised 2023-24 Some Basic Concepts of Chemistry 5 (iii) Gases have neither definite volume nor definite shape. They completely occupy the space in the container in which they are placed. These three states of matter are interconvertible by changing the conditions of temperature and pressure. Solid liquid Gas On heating, a solid usually changes to a liquid, and the liquid on further heating changes to gas (or vapour). In the reverse process, a gas on cooling liquifies to the liquid and the liquid on further cooling freezes to the solid. 1.2.2. Classification of Matter In Class IX (Chapter 2), you have learnt that at the macroscopic or bulk level, matter can be classified as mixture or pure substance. These can be further sub-divided as shown in Fig. 1.2. When all constituent particles of a substance are same in chemical nature, it is said to be a pure substance. A mixture contains many types of particles. A mixture contains particles of two or more pure substances which may be present in it in any ratio. Hence, their composition is variable. Pure substances forming mixture are called its components. Many of the substances present around you are mixtures. For example, sugar solution in water, air, tea, etc., are all mixtures. A mixture may be homogeneous or heterogeneous. In a homogeneous mixture, the components Fig. 1.2 Classification of matter Fig. 1.1 Arrangement of particles in solid, liquid and gaseous state completely mix with

each other. This means particles of components of the mixture are uniformly distributed throughout the bulk of the mixture and its composition is uniform throughout. Sugar solution and air are the examples of homogeneous mixtures. In contrast to this, in a heterogeneous mixture, the composition is not uniform throughout and sometimes different components are visible. For example, mixtures of salt and sugar, grains and pulses along with some dirt (often stone pieces), are heterogeneous mixtures. You can think of many more examples of mixtures which you come across in the daily life. It is worthwhile to mention here that the components of a mixture can be separated by using physical methods, such as simple hand-picking, filtration, crystallisation, distillation, etc. Pure substances have characteristics different from mixtures. Constituent particles of pure substances have fixed composition. Copper, silver, gold, water and glucose are some examples of pure substances. Glucose contains carbon, hydrogen and oxygen in a fixed ratio and its particles are of same composition. Hence, like all other pure substances, glucose has a fixed composition. Also, its constituents—carbon, hydrogen and oxygen—cannot be separated by simple physical methods. Pure substances can further be classified into elements and compounds. Particles of an element consist of only one type of atoms. These particles may exist as atoms or molecules. You may be familiar with atoms Rationalised 2023-24 6 chemistry and molecules from the previous classes; however, you will be studying about them in detail in Unit 2. Sodium, copper, silver, hydrogen, oxygen, etc., are some examples of elements. Their all atoms are of one type. However, the atoms of different elements are different in nature. Some elements, such as sodium or copper, contain atoms as their constituent particles, whereas, in some others, the constituent particles are molecules which are formed by two or more atoms. For example, hydrogen, nitrogen and oxygen gases consist of molecules, in which two atoms combine to give their respective molecules. This is illustrated in Fig. 1.3. elements are present in a compound in a fixed and definite ratio and this ratio is characteristic of a particular compound. Also, the properties of a compound are different from those of its constituent elements. For example, hydrogen and oxygen are gases, whereas, the compound formed by their combination i.e., water is a liquid. It is interesting to note that hydrogen burns with a pop sound and oxygen is a supporter of combustion, but water is used as a fire extinguisher. 1.3 Properties of Matter and their Measurement 1.3.1 Physical and chemical properties Every substance has unique or characteristic properties. These properties can be classified into two categories — physical properties, such as colour, odour, melting point, boiling point, density, etc., and chemical properties, like composition, combustibility, ractivity with acids and bases, etc. Physical properties can be measured or observed without changing the identity or the composition of the substance. The measurement or observation of chemical properties requires a chemical change to occur. Measurement of physical properties does not require occurance of a chemical change. The examples of chemical properties are characteristic reactions of different substances; these include acidity or basicity, combustibility, etc. Chemists describe, interpret and predict the behaviour of substances on the basis of knowledge of their physical and chemical properties, which are determined by careful measurement and experimentation. In the following section, we When two or more atoms of different elements combine together in a definite ratio, the molecule of a compound is obtained. Moreover, the constituents of a compound cannot be separated into simpler substances by physical methods. They can be separated by chemical methods. Examples of some compounds are water, ammonia, carbon dioxide, sugar, etc. The molecules of water and carbon dioxide are represented in Fig. 1.4. Note that a water molecule comprises two hydrogen atoms and one oxygen atom. Similarly, a molecule of carbon dioxide contains two oxygen atoms combined with one carbon atom. Thus, the atoms of different Fig. 1.4 A depiction of molecules of water and carbon dioxide Water molecule ($H_2O$) Carbon dioxide molecule ($CO_2$) Fig. 1.3 A representation of atoms and molecules Rationalised 2023-24 Some Basic Concepts of Chemistry 7 will learn about the measurement of physical properties. 1.3.2 Measurement of physical properties Quantitative measurement of properties is reaquired for

scientific investigation. Many properties of matter, such as length, area, volume, etc., are quantitative in nature. Any quantitative observation or measurement is represented by a number followed by units in which it is measured. For example, length of a room can be represented as 6 m; here, 6 is the number and m denotes metre, the unit in which the length is measured. Earlier, two different systems of measurement, i.e., the English System and the Metric System were being used in different parts of the world. The metric system, which originated in France in late eighteenth century, was more convenient as it was based on the decimal system. Late, need of a common standard system was felt by the scientific community. Such a system was established in 1960 and is discussed in detail below. 1.3.3 The International System of Units (SI) The International System of Units (in French Le Systeme International d'Unités — abbreviated as SI) was established by the 11th General Conference on Weights and Measures (CGPM from Conference Generale des Poids et Measures). The CGPM is an intergovernmental treaty organisation created by a diplomatic treaty known as Metre Convention, which was signed in Paris in 1875. The SI system has seven base units and they are listed in Table 1.1. These units pertain to the seven fundamental scientific quantities. The other physical quantities, such as speed, volume, density, etc., can be derived from these quantities. Maintaining the National Standards of Measurement The system of units, including unit definitions, keeps on changing with time. Whenever the accuracy of measurement of a particular unit was enhanced substantially by adopting new principles, member nations of metre treaty (signed in 1875), agreed to change the formal definition of that unit. Each modern industrialised country, including India, has a National Metrology Institute (NMI), which maintains standards of measurements. This responsibility has been given to the National Physical Laboratory (NPL), New Delhi. This laboratory establishes experiments to realise the base units and derived units of measurement and maintains National Standards of Measurement. These standards are periodically inter-compared with standards maintained at other National Metrology Institutes in the world, as well as those, established at the International Bureau of Standards in Paris. Table 1.1 Base Physical Quantities and their Units Base Physical Quantity Symbol for Quantity Name of SI Unit Symbol for SI Unit Length Mass Time Electric current Thermodynamic temperature Amount of substance Luminous intensity l m t I T n I v metre kilogram second ampere kelvin mole candela m kg s A K mol cd Rationalised 2023-24 8 chemistry These prefixes are listed in Table 1.3. Let us now quickly go through some of the quantities which you will be often using in this book. The definitions of the SI base units are given in Table 1.2. The SI system allows the use of prefixes to indicate the multiples or submultiples of a unit. Table 1.2 Definitions of SI Base Units Unit of length metre The metre, symbol m is the SI unit of length. It is defined by taking the fixed numerical value of the speed of light in vacuum c to be 299792458 when expressed in the unit $ms^{-1}$, where the second is defined in terms of the caesium frequency $\Delta$Cs. Unit of mass kilogram The kilogram, symbol kg. is the SI unit of mass. It is defined by taking the fixed numerical value of the planck constant h to be $6.62607015 \times 10^{-34}$ when expressed in the unit Js, which is equal to $kgm^2s^{-1}$, where the metre and the second are defined in terms of c and$\Delta$Cs. Unit of time second The second symbol s, is the SI unit of time. It is defined by taking the fixed numerical value of the caesium frequency $\Delta$Cs, the unperturbed ground-state hyperfine transition frequency of the caesium-133 atom, to be 9192631770 when expressed in the unit Hz, which is equal to $s^{-1}$. Unit of electric current ampere The ampere, symbol A, is the SI unit of electric current. It is defined by taking the fixed numerical value of the elementary charge e to be $1.602176634 \times 10^{-19}$ when expressed in the unit C, which is equal to As, where the second is defined in terms of $\Delta$Cs. Unit of thermodynamic temperature kelvin The kelvin, symbol k, is the SI unit of thermodynamic temperature. It is defined by taking the fixed numerical value of the Boltzmann constant k to be $1.380649 \times 10^{-23}$ when expressed in the unit $JK^{-1}$, which is equal to $kgm^2s^{-2}k^{-1}$ where the kilogram, metre and second are defined in terms of h, c and $\Delta$Cs. Unit of amount of substance mole The mole, symbol mol, is the SI unit of amount of substance. One mole contains exactly $6.02214076 \times 10^{23}$ elementary entities. This

number is the fixed numerical value of the Avogadro constant, $N_A$, when expressed in the unit mol$^{-1}$ and is called the Avogadro number. The amount of substance, symbol n, of a system is a measure of the number of specified elementary entities. An elementary entity may be an atom, a molecule, an ion, an electron, any other particle or specified group of particles. Unit of luminous Intensity Candela The candela, symbol cd is the SI unit of luminous intensity in a given direction. It is defined by taking the fixed numerical value of the luminous efficacy of monochromatic radiation of frequency $540 \times 10^{12}$ Hz, $K_{cd}$, to be 683 when expressed in the unit lm·W$^{-1}$, which is equal to cd·sr·W$^{-1}$, or cd sr kg$^{-1}$ m$^{-2}$s$^3$, where the kilogram, metre and second are defined in terms of h, c and V Cs. Rationalised 2023-24 Some Basic Concepts of Chemistry 9 Fig. 1.5 Analytical balance 1.3.4 Mass and Weight Mass of a substance is the amount of matter present in it, while weight is the force exerted by gravity on an object. The mass of a substance is constant, whereas, its weight may vary from one place to another due to change in gravity. You should be careful in using these terms. The mass of a substance can be determined accurately in the laboratory by using an analytical balance (Fig. 1.5). The SI unit of mass as given in Table 1.1 is kilogram. However, its fraction named as gram (1 kg = 1000 g), is used in laboratories due to the smaller amounts of chemicals used in chemical reactions. 1.3.5 Volume Volume is the amont of space occupied by a substance. It has the units of (length)$^3$. So in SI system, volume has units of m$^3$. But again, in chemistry laboratories, smaller volumes are used. Hence, volume is often denoted in cm$^3$ or dm$^3$ units. A common unit, litre (L) which is not an SI unit, is used for measurement of volume of liquids. 1 L = 1000 mL, 1000 cm$^3$ = 1 dm$^3$ Fig. 1.6 helps to visualise these relations. Fig. 1.6 Different units used to express volume Table 1.3 Prefixes used in the SI System Multiple Prefix Symbol $10^{-24}$ $10^{-21}$ $10^{-18}$ $10^{-15}$ $10^{-12}$ $10^{-9}$ $10^{-6}$ $10^{-3}$ $10^{-2}$ $10^{-1}$ 10 $10^2$ $10^3$ $10^6$ $10^9$ $10^{12}$ $10^{15}$ $10^{18}$ $10^{21}$ $10^{24}$ yocto zepto atto femto pico nano micro milli centi deci deca hecto kilo mega giga tera peta exa zeta yotta y z a f p n $\mu$ m c d da h k M G T P E Z Y Rationalised 2023-24 10 chemistry In the laboratory, the volume of liquids or solutions can be measured by graduated cylinder, burette, pipette, etc. A volumetric flask is used to prepare a known volume of a solution. These measuring devices are shown in Fig. 1.7. Fig. 1.7 Some volume measuring devices 1.4 Uncertainty in Measurement Many a time in the study of chemistry, one has to deal with experimental data as well as theoretical calculations. There are meaningful ways to handle the numbers conveniently and fahrenheit) and K (kelvin). Here, K is the SI unit. The thermometers based on these scales are shown in Fig. 1.8. Generally, the thermometer with celsius scale are calibrated from 0° to 100°, where these two temperatures are the freezing point and the boiling point of water, respectively. The fahrenheit scale is represented between 32° to 212°. The temperatures on two scales are related to each other by the following relationship: $°F = \dfrac{9}{5}(°C) + 32$ The kelvin scale is related to celsius scale as follows: K = °C + 273.15 It is interesting to note that temperature below 0 °C (i.e., negative values) are possible in Celsius scale but in Kelvin scale, negative temperature is not possible. Fig. 1.8 Thermometers using different temperature scales 1.3.6 Density The two properties — mass and volume discussed above are related as follows: Density $= \dfrac{\text{Mass}}{\text{Volume}}$ Density of a substance is its amount of mass per unit volume. So, SI units of density can be obtained as follows: SI unit of density $= \dfrac{\text{kg}}{\text{m}^3}$ = kg m$^3$ or kg m$^{-3}$ This unit is quite large and a chemist often expresses density in g cm$^{-3}$, where mass is expressed in gram and volume is expressed in cm$^3$. Density of a substance tells us about how closely its particles are packed. If density is more, it means particles are more closely packed. 1.3.7 Temperature There are three common scales to measure temperature — °C (degree celsius), °F (degree Rationalised 2023-24 Some Basic Concepts of Chemistry 11 present the data realistically with certainty to the extent possible. These ideas are discussed below in detail. 1.4.1 Scientific Notation As chemistry is the study of atoms and molecules, which have extremely low masses and are present in extremely large numbers, a chemist has to deal with numbers as large as 602, 200,000,000,000,000,000,000 for the molecules of 2 g of hydrogen gas or as small as 0.00000000000000000000000166 g mass of a H atom. Similarly, other constants such as Planck's

constant, speed of light, charges on particles, etc., involve numbers of the above magnitude. It may look funny for a moment to write or count numbers involving so many zeros but it offers a real challenge to do simple mathematical operations of addition, subtraction, multiplication or division with such numbers. You can write any two numbers of the above type and try any one of the operations you like to accept as a challenge, and then, you will really appreciate the difficulty in handling such numbers. This problem is solved by using scientific notation for such numbers, i.e., exponential notation in which any number can be represented in the form $N \times 10^n$, where n is an exponent having positive or negative values and N is a number (called digit term) which varies between 1.000... and 9.999.... Thus, we can write 232.508 as $2.32508 \times 10^2$ in scientific notation. Note that while writing it, the decimal had to be moved to the left by two places and same is the exponent (2) of 10 in the scientific notation. Similarly, 0.00016 can be written as $1.6 \times 10^{-4}$. Here, the decimal has to be moved four places to the right and (−4) is the exponent in the scientific notation. While performing mathematical operations on numbers expressed in scientific notations, the following points are to be kept in mind. Reference Standard After defining a unit of measurement such as the kilogram or the metre, scientists agreed on reference standards that make it possible to calibrate all measuring devices. For getting reliable measurements, all devices such as metre sticks and analytical balances have been calibrated by their manufacturers to give correct readings. However, each of these devices is standardised or calibrated against some reference. The mass standard is the kilogram since 1889. It has been defined as the mass of platinum-iridium (Pt-Ir) cylinder that is stored in an airtight jar at International Bureau of Weights and Measures in Sevres, France. Pt-Ir was chosen for this standard because it is highly resistant to chemical attack and its mass will not change for an extremely long time. Scientists are in search of a new standard for mass. This is being attempted through accurate determination of Avogadro constant. Work on this new standard focuses on ways to measure accurately the number of atoms in a well-defined mass of sample. One such method, which uses X-rays to determine the atomic density of a crystal of ultrapure silicon, has an accuracy of about 1 part in $10^6$ but has not yet been adopted to serve as a standard. There are other methods but none of them are presently adequate to replace the Pt-Ir cylinder. No doubt, changes are expected within this decade. The metre was originally defined as the length between two marks on a Pt-Ir bar kept at a temperature of 0°C (273.15 K). In 1960 the length of the metre was defined as $1.65076373 \times 10^6$ times the wavelength of light emitted by a krypton laser. Although this was a cumbersome number, it preserved the length of the metre at its agreed value. The metre was redefined in 1983 by CGPM as the length of path travelled by light in vacuum during a time interval of 1/299 792 458 of a second. Similar to the length and the mass, there are reference standards for other physical quantities. Rationalised 2023-24 12 chemistry Multiplication and Division These two operations follow the same rules which are there for exponential numbers, i.e. mass obtained by an analytical balance is slightly higher than the mass obtained by using a platform balance. Therefore, digit 4 placed after decimal in the measurement by platform balance is uncertain. The uncertainty in the experimental or the calculated values is indicated by mentioning the number of significant figures. Significant figures are meaningful digits which are known with certainty plus one which is estimated or uncertain. The uncertainty is indicated by writing the certain digits and the last uncertain digit. Thus, if we write a result as 11.2 mL, we say the 11 is certain and 2 is uncertain and the uncertainty would be +1 in the last digit. Unless otherwise stated, an uncertainty of +1 in the last digit is always understood. There are certain rules for determining the number of significant figures. These are stated below: (1) All non-zero digits are significant. For example in 285 cm, there are three significant figures and in 0.25 mL, there are two significant figures. (2) Zeros preceding to first non-zero digit are not significant. Such zero indicates the position of decimal point. Thus, 0.03 has one significant figure and 0.0052 has two significant figures. (3) Zeros between two non-zero digits are significant. Thus, 2.005 has four significant figures. (4) Zeros at the end or right of

a number are significant, provided they are on the right side of the decimal point. For example, 0.200 g has three significant figures. But, if otherwise, the terminal zeros are not significant if there is no decimal point. For example, 100 has only one significant figure, but 100 has three significant figures and 100.0 has four significant figures. Such numbers are better represented in scientific notation. We can express the number 100 as $1 \times 10^2$ for one significant figure, $1.0 \times 10^2$ for two significant figures and $1.00 \times 10^2$ for three significant figures. Addition and Subtraction For these two operations, first the numbers are written in such a way that they have the same exponent. After that, the coefficients (digit terms) are added or subtracted as the case may be. Thus, for adding $6.65 \times 10^4$ and $8.95 \times 10^3$, exponent is made same for both the numbers. Thus, we get $(6.65 \times 10^4) + (0.895 \times 10^4)$ Then, these numbers can be added as follows $(6.65 + 0.895) \times 10^4 = 7.545 \times 10^4$ Similarly, the subtraction of two numbers can be done as shown below: $(2.5 \times 10^{-2}) - (4.8 \times 10^{-3}) = (2.5 \times 10^{-2}) - (0.48 \times 10^{-2}) = (2.5 - 0.48) \times 10^{-2} = 2.02 \times 10^{-2}$ 1.4.2 Significant Figures Every experimental measurement has some amount of uncertainty associated with it because of limitation of measuring instrument and the skill of the person making the measurement. For example, mass of an object is obtained using a platform balance and it comes out to be 9.4g. On measuring the mass of this object on an analytical balance, the mass obtained is 9.4213g. The 5 6 10 6 9 10 56 69 10 56 69 10 5 8 5 8 13 . . . . . . - ⬜ - ⬜- ⬜- ⬜- ⬜ ⬜ = = = 38.64 10 = 3.864 10 = 13 14 - ⬜ - ⬜ - ⬜⬜⬜⬜⬜⬜ 9 8 10 2 5 10 98 25 10 2 6 2 . . . . . 6 2 6 3 98 25 10 2 7 10 5 - ⬜⬜⬜⬜⬜ - ⬜- ⬜- ⬜ = = 24.50 10 = 2.450 10 8 7 . . . .5 10 27 55 10 1 4 3 4 - ⬜⬜- ⬜ ⬜ ⬜ ⬜ ⬜ = =0.4909 0 =4.909 10 7 8 . . Rationalised 2023-24 Some Basic Concepts of Chemistry 13 (5) Counting the numbers of object, for example, 2 balls or 20 eggs, have infinite significant figures as these are exact numbers and can be represented by writing infinite number of zeros after placing a decimal i.e., 2 = 2.000000 or 20 = 20.000000. In numbers written in scientific notation, all digits are significant e.g., $4.01 \times 10^2$ has three significant figures, and $8.256 \times 10^{-3}$ has four significant figures. However, one would always like the results to be precise and accurate. Precision and accuracy are often referred to while we talk about the measurement. Precision refers to the closeness of various measurements for the same quantity. However, accuracy is the agreement of a particular value to the true value of the result. For example, if the true value for a result is 2.00 g and student 'A' takes two measurements and reports the results as 1.95 g and 1.93 g. These values are precise as they are close to each other but are not accurate. Another student 'B' repeats the experiment and obtains 1.94 g and 2.05 g as the results for two measurements. These observations are neither precise nor accurate. When the third student 'C' repeats these measurements and reports 2.01 g and 1.99 g as the result, these values are both precise and accurate. This can be more clearly understood from the data given in Table 1.4.

Table 1.4 Data to Illustrate Precision and Accuracy

| | Measurements/g | | Average (g) |
|---|---|---|---|
| | 1 | 2 | |
| Student A | 1.95 | 1.93 | 1.940 |
| Student B | 1.94 | 2.05 | 1.995 |
| Student C | 2.01 | 1.99 | 2.000 |

Addition and Subtraction of Significant Figures The result cannot have more digits to the right of the decimal point than either of the original numbers.
12.11
18.0
1.012
31.122
Here, 18.0 has only one digit after the decimal point and the result should be reported only up to one digit after the decimal point, which is 31.1. Multiplication and Division of Significant Figures In these operations, the result must be reported with no more significant figures as in the measurement with the few significant figures.
$2.5 \times 1.25 = 3.125$ Since 2.5 has two significant figures, the result should not have more than two significant figures, thus, it is 3.1. While limiting the result to the required number of significant figures as done in the above mathematical operation, one has to keep in mind the following points for rounding off the numbers 1. If the rightmost digit to be removed is more than 5, the preceding number is increased by one. For example, 1.386. If we have to remove 6, we have to round it to 1.39. 2. If the rightmost digit to be removed is less than 5, the preceding number is not changed. For example, 4.334 if 4 is to be removed, then the result is rounded upto 4.33. 3. If the rightmost digit to be removed is 5, then the preceding number is not changed if it is an even number but it is increased by one if it is an odd number. For example, if 6.35 is to be rounded by removing 5, we have to

increase 3 to 4 giving 6.4 as the result. However, if 6.25 is to be rounded off it is rounded off to 6.2.

1.4.3 Dimensional Analysis Often while calculating, there is a need to convert units from one system to the other. The method used to accomplish this is called factor label method or unit factor method or dimensional analysis. This is illustrated below. Example A piece of metal is 3 inch (represented by in) long. What is its length in cm? Rationalised 2023-24 14 chemistry Solution We know that 1 in = 2.54 cm From this equivalence, we can write Thus, 1 2 54 in . cm equals 1 and 2 54 1 . cm in also equals 1. Both of these are called unit factors. If some number is multiplied by these unit factors (i.e., 1), it will not be affected otherwise. Say, the 3 in given above is multiplied by the unit factor. So, 3 in = 3 in × 2 54 1 . cm in = 3 × 2.54 cm = 7.62cm Now, the unit factor by which multiplication is to be done is that unit factor ( 2 54 1 . cm in in the above case) which gives the desired units i.e., the numerator should have that part which is required in the desired result. It should also be noted in the above example that units can be handled just like other numerical part. It can be cancelled, divided, multiplied, squared, etc. Let us study one more example. Example A jug contains 2L of milk. Calculate the volume of the milk in m3. Solution Since 1 L = 1000 cm3 and 1m = 100 cm, which gives 1 100 1 100 1 m cm cm m = = To get m3 from the above unit factors, the first unit factor is taken and it is cubed. 1 100 1 10 1 1 3 3 6 3 m 3 cm m cm  -            Now 2 L = 2 ×1000 cm3 1 2 54 1 2 54 1 in cm cm . in . = = The above is multiplied by the unit factor 2 1000 1 10 2 10 2 10 3 3 6 3 3 3 3  - -   cm m cm m m m Example How many seconds are there in 2 days? Solution Here, we know 1 day = 24 hours (h) or 1 24 1 24 1 day h h day = = then, 1h = 60 min or 1 60 1 60 1 h min h min = = so, for converting 2 days to seconds, i.e., 2 days − − − − − = − − − seconds The unit factors can be multiplied in series in one step only as follows: 2 24 1 60 1 60 1 day h day h s × × × min min = 2 × 24 × 60 × 60 s = 172800 s 1.5 Laws of Chemical Combinations The combination of elements to form compounds is governed by the following five basic laws. 1.5.1 Law of Conservation of Mass This law was put forth by Antoine Lavoisier in 1789. He performed careful experimental studies for combustion reactions and reached to the conclusion that in all physical and chemical changes, there is no net change in mass duting the process. Hence, he reached to the conclusion that matter can neither be created nor destroyed. This is called 'Law of Conservation of Mass'. This law formed the basis for several later developments in chemistry. Infact, this was the result of exact measurement of masses of reactants and products, and carefully planned experiments performed by Lavoisier. Antoine Lavoisier (1743–1794) Rationalised 2023-24 Some Basic Concepts of Chemistry 15 are produced in a chemical reaction they do so in a simple ratio by volume, provided all gases are at the same temperature and pressure. Thus, 100 mL of hydrogen combine with 50 mL of oxygen to give 100 mL of water vapour. Hydrogen + Oxygen → Water 100 mL 50 mL 100 mL Thus, the volumes of hydrogen and oxygen which combine (i.e., 100 mL and 50 mL) bear a simple ratio of 2:1. Gay Lussac's discovery of integer ratio in volume relationship is actually the law of definite proportions by volume. The law of definite proportions, stated earlier, was with respect to mass. The Gay Lussac's law was explained properly by the work of Avogadro in 1811. 1.5.5 Avogadro's Law In 1811, Avogadro proposed that equal volumes of all gases at the same temperature and pressure should contain equal number of molecules. Avogadro made a distinction between atoms and molecules which is quite understandable in present times. If we consider again the reaction of hydrogen and oxygen to produce water, we see that two volumes of hydrogen combine with one volume of oxygen to give two volumes of water without leaving any unreacted oxygen. Note that in the Fig. 1.9 (Page 16) each box contains equal number of molecules. In fact, Avogadro could explain the above result by considering the molecules to be polyatomic. If hydrogen and oxygen were considered as diatomic as recognised now, then the above results are easily understandable. However, Dalton and others believed at that time that atoms of the same kind 1.5.2 Law of Definite Proportions This law was given by, a French chemist, Joseph Proust. He stated that a given compound always contains exactly the same proportion of elements by weight. Proust worked with two samples of cupric carbonate — one of which was of natural origin

and the other was synthetic. He found that the composition of elements present in it was same for both the samples as shown below: % of copper % of carbon % of oxygen Natural Sample Synthetic Sample 51.35 51.35 9.74 9.74 38.91 38.91 Thus, he concluded that irrespective of the source, a given compound always contains same elements combined together in the same proportion by mass. The validity of this law has been confirmed by various experiments. It is sometimes also referred to as Law of Definite Composition. 1.5.3 Law of Multiple Proportions This law was proposed by Dalton in 1803. According to this law, if two elements can combine to form more than one compound, the masses of one element that combine with a fixed mass of the other element, are in the ratio of small whole numbers. For example, hydrogen combines with oxygen to form two compounds, namely, water and hydrogen peroxide. Hydrogen + Oxygen → Water 2g 16g 18g Hydrogen + Oxygen → Hydrogen Peroxide 2g 32g 34g Here, the masses of oxygen (i.e., 16 g and 32 g), which combine with a fixed mass of hydrogen (2g) bear a simple ratio, i.e., 16:32 or 1: 2. 1.5.4 Gay Lussac's Law of Gaseous Volumes This law was given by Gay Lussac in 1808. He observed that when gases combine or Joseph Proust (1754–1826) Joseph Louis Gay Lussac Lorenzo Romano Amedeo Carlo Avogadro di Quareqa edi Carreto (1776–1856) Rationalised 2023-24 16 chemistry cannot combine and molecules of oxygen or hydrogen containing two atoms did not exist. Avogadro's proposal was published in the French Journal de Physique. In spite of being correct, it did not gain much support. After about 50 years, in 1860, the first international conference on chemistry was held in Karlsruhe, Germany, to resolve various ideas. At the meeting, Stanislao Cannizaro presented a sketch of a course of chemical philosophy, which emphasised on the importance of Avogadro's work. 1.6 Dalton's Atomic Theory Although the origin of the idea that matter is composed of small indivisible particles called 'a-tomio' (meaning, indivisible), dates back to the time of Democritus, a Greek Philosopher (460– 370 BC), it again started emerging as a result of several experimental studies which led to the laws mentioned above. In 1808, Dalton published 'A New System of Chemical Philosophy', in which he proposed the following : 1. Matter consists of indivisible atoms. 2. All atoms of a given element have identical properties, including identical mass. Atoms of different elements differ in mass. 3. Compounds are formed when atoms of different elements combine in a fixed ratio. 4. Chemical reactions involve reorganisation of atoms. These are neither created nor destroyed in a chemical reaction. Dalton's theory could explain the laws of chemical combination. However, it could not explain the laws of gaseous volumes. It could not provide the reason for combining of atoms, which was answered later by other scientists. 1.7 Atomic and Molecular Masses After having some idea about the terms atoms and molecules, it is appropriate here to understand what do we mean by atomic and molecular masses. 1.7.1 Atomic Mass The atomic mass or the mass of an atom is actually very-very small because atoms are extremely small. Today, we have sophisticated techniques e.g., mass spectrometry for determining the atomic masses fairly accurately. But in the nineteenth century, scientists could determine the mass of one atom relative to another by experimental means, as has been mentioned earlier. Hydrogen, being the lightest atom was arbitrarily assigned a mass of 1 (without any units) and other elements were assigned masses relative to it. However, the present system of atomic masses is based on carbon-12 as the standard and has been agreed upon in 1961. Here, Carbon-12 is one of the isotopes of carbon and can be represented as 12C. In this system, 12C is assigned a mass of exactly 12 atomic mass unit (amu) and masses of all other atoms are given relative to this standard. One atomic mass unit is defined as a mass exactly equal to one-twelfth of the mass of one carbon – 12 atom. John Dalton (1776–1884) Fig. 1.9 Two volumes of hydrogen react with one volume of oxygen to give two volumes of water vapour Rationalised 2023-24 Some Basic Concepts of Chemistry 17 And 1 amu = $1.66056 \times 10^{-24}$ g Mass of an atom of hydrogen = $1.6736 \times 10^{-24}$ g Thus, in terms of amu, the mass of hydrogen atom = = 1.0078 amu = 1.0080 amu Similarly, the mass of oxygen - 16 (16O) atom would be 15.995 amu. At present, 'amu' has been replaced by 'u', which is known as unified mass. When we use atomic masses of elements in calculations, we actually

use average atomic masses of elements, which are explained below. 1.7.2 Average Atomic Mass Many naturally occurring elements exist as more than one isotope. When we take into account the existence of these isotopes and their relative abundance (per cent occurrence), the average atomic mass of that element can be computed. For example, carbon has the following three isotopes with relative abundances and masses as shown against each of them. Isotope Relative Abundance (%) Atomic Mass (amu) 12C 13C 14C 98.892 1.108 2 ×10–10 12 13.00335 14.00317 From the above data, the average atomic mass of carbon will come out to be: (0.98892) (12 u) + (0.01108) (13.00335 u) + (2 ×10–12) (14.00317 u) = 12.011 u Similarly, average atomic masses for other elements can be calculated. In the periodic table of elements, the atomic masses mentioned for different elements actually represent their average atomic masses. 1.7.3 Molecular Mass Molecular mass is the sum of atomic masses of the elements present in a molecule. It is obtained by multiplying the atomic mass of each element by the number of its atoms and adding them together. For example, molecular mass of methane, which contains one carbon atom and four hydrogen atoms, can be obtained as follows: Molecular mass of methane, $(CH_4)$ = (12.011 u) + 4 (1.008 u) = 16.043 u Similarly, molecular mass of water $(H_2O)$ = 2 × atomic mass of hydrogen + 1× atomic mass of oxygen = 2 (1.008 u) + 16.00 u = 18.02 u 1.7.4 Formula Mass Some substances, such as sodium chloride, do not contain discrete molecules as their constituent units. In such compounds, positive (sodium ion) and negative (chloride ion) entities are arranged in a three-dimensional structure, as shown in Fig. 1.10. It may be noted that in sodium chloride, one $Na^+$ ion is surrounded by six $Cl^-$ ion and vice-versa. The formula, such as NaCl, is used to calculate the formula mass instead of molecular mass as in the solid state sodium chloride does not exist as a single entity. Fig. 1.10 Packing of $Na^+$ and $Cl^-$ ions in sodium chloride Rationalised 2023-24 18 chemistry This number of entities in 1 mol is so important that it is given a separate name and symbol. It is known as 'Avogadro constant', or Avogadro number denoted by $N_A$ in honour of Amedeo Avogadro. To appreciate the largeness of this number, let us write it with all zeroes without using any powers of ten. 602213670000000000000000 Hence, so many entities (atoms, molecules or any other particle) constitute one mole of a particular substance. We can, therefore, say that 1 mol of hydrogen atoms = 6.022 ×1023 atoms 1 mol of water molecules = 6.022 ×1023 water molecules 1 mol of sodium chloride = 6.022×1023 formula units of sodium chloride Having defined the mole, it is easier to know the mass of one mole of a substance or the constituent entities. The mass of one mole of a substance in grams is called its molar mass. The molar mass in grams is numerically equal to atomic/molecular/ formula mass in u. Molar mass of water = 18.02 g mol–1 Molar mass of sodium chloride = 58.5 g mol–1 1.9 Percentage Composition So far, we were dealing with the number of entities present in a given sample. But many a time, information regarding the percentage of a particular element present in a compound is required. Suppose, an unknown or new compound is given to you, the first question Fig. 1.11 One mole of various substances Thus, the formula mass of sodium chloride is atomic mass of sodium + atomic mass of chlorine = 23.0 u + 35.5 u = 58.5 u Problem 1.1 Calculate the molecular mass of glucose $(C_6H_{12}O_6)$ molecule. Solution Molecular mass of glucose $(C_6H_{12}O_6)$ = 6 (12.011 u) + 12 (1.008 u) + 6 (16.00 u) = (72.066 u) + (12.096 u) + (96.00 u) = 180.162 u 1.8 Mole concept and Molar Masses Atoms and molecules are extremely small in size and their numbers in even a small amount of any substance is really very large. To handle such large numbers, a unit of convenient magnitude is required. Just as we denote one dozen for 12 items, score for 20 items, gross for 144 items, we use the idea of mole to count entities at the microscopic level (i.e., atoms, molecules, particles, electrons, ions, etc). In SI system, mole (symbol, mol) was introduced as seventh base quantity for the amount of a substance. The mole, symbol mol, is the SI unit of amount of substance. One mole contains exactly 6.02214076 ×1023 elementary entities. This number is the fixed numerical value of the Avogadro constant, $N_A$, when expressed in the unit mol–1 and is called the Avogadro number. The amount of substance, symbol n, of a system is a measure of the number of specified elementary entities. An elementary

entity may be an atom, a molecule, an ion, an electron, any other particle or specified group of particles. It may be emphasised that the mole of a substance always contains the same number of entities, no matter what the substance may be. In order to determine this number precisely, the mass of a carbon–12 atom was determined by a mass spectrometer and found to be equal to $1.992648 \times 10^{-23}$ g. Knowing that one mole of carbon weighs 12 g, the number of atoms in it is equal to:

$$\frac{12 \text{ g mol}^{-1} \text{ C}}{1.992648 \times 10^{-23} \text{ g/Catom}} = 6.0221367 \times 10^{23} \text{ atoms/mol}$$

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you would ask is: what is its formula or what are its constituents and in what ratio are they present in the given compound? For known compounds also, such information provides a check whether the given sample contains the same percentage of elements as present in a pure sample. In other words, one can check the purity of a given sample by analysing this data. Let us understand it by taking the example of water (H2O). Since water contains hydrogen and oxygen, the percentage composition of both these elements can be calculated as follows: Mass % of an element = mass of that element in the compound $\times \frac{100}{\text{molar mass of the compound}}$ Molar mass of water = 18.02 g Mass % of hydrogen = $= 11.18$ Mass % of oxygen = $\frac{16.00}{18.02} \times 100 = 88.79$ Let us take one more example. What is the percentage of carbon, hydrogen and oxygen in ethanol? Molecular formula of ethanol is: C2H5OH Molar mass of ethanol is: $(2 \times 12.01 + 6 \times 1.008 + 16.00)$ g = 46.068 g Mass per cent of carbon = $\frac{24.02 g}{46.068 g} \times 100 = 52.14\%$ Mass per cent of hydrogen = $\frac{6.048 g}{46.068 g} \times 100 = 13.13\%$ Mass per cent of oxygen = $\frac{16.00 g}{46.068 g} \times 100 = 34.73\%$ After understanding the calculation of per cent of mass, let us now see what information can be obtained from the per cent composition data.

1.9.1 Empirical Formula for Molecular Formula An empirical formula represents the simplest whole number ratio of various atoms present in a compound, whereas, the molecular formula shows the exact number of different types of atoms present in a molecule of a compound. If the mass per cent of various elements present in a compound is known, its empirical formula can be determined. Molecular formula can further be obtained if the molar mass is known. The following example illustrates this sequence. Problem 1.2 A compound contains 4.07% hydrogen, 24.27% carbon and 71.65% chlorine. Its molar mass is 98.96 g. What are its empirical and molecular formulas? Solution Step 1. Conversion of mass per cent to grams Since we are having mass per cent, it is convenient to use 100 g of the compound as the starting material. Thus, in the 100 g sample of the above compound, 4.07g hydrogen, 24.27g carbon and 71.65g chlorine are present. Step 2. Convert into number moles of each element Divide the masses obtained above by respective atomic masses of various elements. This gives the number of moles of constituent elements in the compound Moles of hydrogen = $\frac{4.07 g}{1.008 g} = 4.04$ Moles of carbon = $\frac{24.27 g}{12.01 g} = 2.021$ Moles of chlorine = $\frac{71.65 g}{35.453 g} = 2.021$

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equation of a given reaction. Let us consider the combustion of methane. A balanced equation for this reaction is as given below: CH4 (g) + 2O2 (g) → CO2 (g) + 2 H2O (g) Here, methane and dioxygen are called reactants and carbon dioxide and water are called products. Note that all the reactants and the products are gases in the above reaction and this has been indicated by letter (g) in the brackets next to its formula. Similarly, in case of solids and liquids, (s) and (l) are written respectively. The coefficients 2 for O2 and H2O are called stoichiometric coefficients. Similarly the coefficient for CH4 and CO2 is one in each case. They represent the number of molecules (and moles as well) taking part in the reaction or formed in the reaction. Thus, according to the above chemical reaction, • One mole of CH4(g) reacts with two moles of O2(g) to give one mole of CO2(g) and two moles of H2O(g) • One molecule of CH4(g) reacts with 2 molecules of O2(g) to give one molecule of CO2(g) and 2 molecules of H2O(g) • 22.7 L of CH4(g) reacts with 45.4 L of O2 (g) to give 22.7 L of CO2 (g) and 45.4 L of H2O(g) • 16 g of CH4 (g) reacts with 2×32 g of O2 (g) to give 44 g of CO2 (g) and 2×18 g of H2O (g). From these relationships, the given data can be interconverted as follows: $\frac{\text{mass}}{\text{Volume}} = $ Density Mass 1.10.1 Limiting Reagent Many a time, reactions are carried out with the amounts of reactants that are different than the amounts as required by a balanced

chemical reaction. In such situations, one reactant is in more amount than the amount required by balanced chemical reaction. The 1.10 Stoichiometry and Stoichiometric Calculations The word 'stoichiometry' is derived from two Greek words — stoicheion (meaning, element) and metron (meaning, measure). Stoichiometry, thus, deals with the calculation of masses (sometimes volumes also) of the reactants and the products involved in a chemical reaction. Before understanding how to calculate the amounts of reactants required or the products produced in a chemical reaction, let us study what information is available from the balanced chemical Step 3. Divide each of the mole values obtained above by the smallest number amongst them Since 2.021 is smallest value, division by it gives a ratio of 2:1:1 for H:C:Cl. In case the ratios are not whole numbers, then they may be converted into whole number by multiplying by the suitable coefficient. Step 4. Write down the empirical formula by mentioning the numbers after writing the symbols of respective elements $CH_2Cl$ is, thus, the empirical formula of the above compound. Step 5. Writing molecular formula (a) Determine empirical formula mass by adding the atomic masses of various atoms present in the empirical formula. For $CH_2Cl$, empirical formula mass is 12.01 + (2 ×1.008) + 35.453 = 49.48 g (b) Divide Molar mass by empirical formula mass = 2 = (n) (c) Multiply empirical formula by n obtained above to get the molecular formula Empirical formula = $CH_2Cl$, n = 2. Hence molecular formula is $C_2H_4Cl_2$. Rationalised 2023-24 Some Basic Concepts of Chemistry 21 reactant which is present in the least amount gets consumed after sometime and after that further reaction does not take place whatever be the amount of the other reactant. Hence, the reactant, which gets consumed first, limits the amount of product formed and is, therefore, called the limiting reagent. In performing stoichiometric calculations, this aspect is also to be kept in mind. 1.10.2 Reactions in Solutions A majority of reactions in the laboratories are carried out in solutions. Therefore, it is important to understand as how the amount of substance is expressed when it is present in the solution. The concentration of a solution or the amount of substance present in its given volume can be expressed in any of the following ways. 1. Mass per cent or weight per cent (w/w %) 2. Mole fraction 3. Molarity 4. Molality Let us now study each one of them in detail. Balancing a chemical equation According to the law of conservation of mass, a balanced chemical equation has the same number of atoms of each element on both sides of the equation. Many chemical equations can be balanced by trial and error. Let us take the reactions of a few metals and non-metals with oxygen to give oxides 4 Fe(s) + $3O_2$(g) → $2Fe_2O_3$(s) (a) balanced equation 2 Mg(s) + $O_2$(g) → 2MgO(s) (b) balanced equation $P_4$(s) + $O_2$ (g) → $P_4O_{10}$(s) (c) unbalanced equation Equations (a) and (b) are balanced, since there are same number of metal and oxygen atoms on each side of the equations. However equation (c) is not balanced. In this equation, phosphorus atoms are balanced but not the oxygen atoms. To balance it, we must place the coefficient 5 on the left of oxygen on the left side of the equation to balance the oxygen atoms appearing on the right side of the equation. $P_4$(s) + $5O_2$(g) → $P_4O_{10}$(s) balanced equation Now, let us take combustion of propane, $C_3H_8$. This equation can be balanced in steps. Step 1 Write down the correct formulas of reactants and products. Here, propane and oxygen are reactants, and carbon dioxide and water are products. $C_3H_8$(g) + $O_2$(g) → $CO_2$ (g) + $H_2O$(l) unbalanced equation Step 2 Balance the number of C atoms: Since 3 carbon atoms are in the reactant, therefore, three $CO_2$ molecules are required on the right side. $C_3H_8$ (g) + $O_2$ (g) → $3CO_2$ (g) + $H_2O$ (l) Step 3 Balance the number of H atoms: on the left there are 8 hydrogen atoms in the reactants however, each molecule of water has two hydrogen atoms, so four molecules of water will be required for eight hydrogen atoms on the right side. $C_3H_8$ (g) +$O_2$ (g) → $3CO_2$ (g)+$4H_2O$ (l) Step 4 Balance the number of O atoms: There are 10 oxygen atoms on the right side (3 × 2 = 6 in $CO_2$ and 4×1= 4 in water). Therefore, five $O_2$ molecules are needed to supply the required 10 $CO_2$ and 4×1= 4 in water). Therefore, five $O_2$ molecules are needed to supply the required 10 oxygen atoms. $C_3H_8$ (g) +$5O_2$ (g) → $3CO_2$ (g) + $4H_2O$ (l) Step 5 Verify that the number of atoms of each element is balanced in the final equation. The equation shows three carbon atoms, eight hydrogen atoms, and 10 oxygen

atoms on each side. All equations that have correct formulas for all reactants and products can be balanced. Always remember that subscripts in formulas of reactants and products cannot be changed to balance an equation. 22 chemistry Problem 1.3 Calculate the amount of water (g) produced by the combustion of 16 g of methane. Solution The balanced equation for the combustion of methane is : $CH_4$ (g) + $2O_2$ (g) → $CO_2$ (g) + $2H_2O$ (g) (i) 16 g of $CH_4$ corresponds to one mole. (ii) From the above equation, 1 mol of $CH_4$ (g) gives 2 mol of $H_2O$ (g). 2 mol of water ($H_2O$) = 2×(2+16) = 2×18 = 36 g 1 mol $H_2O$ = 18 g $H_2O$ ⇒ 18g H O 1mol H O 2 2 = 1 Hence, 2 mol $H_2O$× 18g H O 1mol H O 2 2 = 2×18 g $H_2O$ = 36 g $H_2O$ Problem 1.4 How many moles of methane are required to produce 22g $CO_2$ (g) after combustion? Solution According to the chemical equation, $CH_4$ (g) + $2O_2$ (g) → $CO_2$ (g) + $2H_2O$ (g) 44g $CO_2$ (g) is obtained from 16 g $CH_4$ (g). [∵1 mol $CO_2$(g) is obtained from 1 mol of $CH_4$(g)] Number of moles of $CO_2$ (g) = 22 g $CO_2$ (g) × 1 44 2 2 mol CO g g CO g $\text{-}$ $\text{-}$ = 0.5 mol $CO_2$ (g) Hence, 0.5 mol $CO_2$ (g) would be obtained from 0.5 mol $CH_4$ (g) or 0.5 mol of $CH_4$ (g) would be required to produce 22 g $CO_2$ (g). Problem 1.5 50.0 kg of $N_2$ (g) and 10.0 kg of $H_2$ (g) are mixed to produce $NH_3$ (g). Calculate the amount of $NH_3$ (g) formed. Identify the limiting reagent in the production of $NH_3$ in this situation. Solution A balanced equation for the above reaction is written as follows : Calculation of moles : Number of moles of $N_2$ = 50 0 1000 1 1 28 0 2 2 2 2 2 . . kg N g N kg N mol N g N × × = $17.86 \times 10^2$ mol Number of moles of $H_2$ = 10 00 1000 1 1 2 016 2 2 2 2 2 . . kg H g H kg H mol H g H × × = $4.96 \times 10^3$ mol According to the above equation, 1 mol $N_2$ (g) requires 3 mol $H_2$ (g), for the reaction. Hence, for $17.86 \times 10^2$ mol of $N_2$, the moles of $H_2$ (g) required would be 17 86 10 3 1 2 2 2 2 . - ☐ - ☐ mol N mol H g mol N g = $5.36 \times 10^3$ mol $H_2$ But we have only $4.96 \times 10^3$ mol $H_2$. Hence, dihydrogen is the limiting reagent in this case. So, $NH_3$(g) would be formed only from that amount of available dihydrogen i.e., $4.96 \times 10^3$ mol Since 3 mol $H_2$(g) gives 2 mol $NH_3$(g) $4.96 \times 10^3$ mol $H_2$ (g) × 2 3 3 2 mol NH g mol H g - - = $3.30 \times 10^3$ mol $NH_3$ (g) $3.30 \times 10^3$ mol $NH_3$ (g) is obtained. If they are to be converted to grams, it is done as follows : 1 mol $NH_3$ (g) = 17.0 g $NH_3$ (g) $3.30 \times 10^3$ mol $NH_3$ (g) × 17 0 1 3 3 . g NH g mol NH g - - Some Basic Concepts of Chemistry 23 3. Molarity It is the most widely used unit and is denoted by M. It is defined as the number of moles of the solute in 1 litre of the solution. Thus, Molarity (M) = No. of moles of solute Volume of solution in litres Suppose, we have 1 M solution of a substance, say NaOH, and we want to prepare a 0.2 M solution from it. 1 M NaOH means 1 mol of NaOH present in 1 litre of the solution. For 0.2 M solution, we require 0.2 moles of NaOH dissolved in 1 litre solution. Hence, for making 0.2M solution from 1M solution, we have to take that volume of 1M NaOH solution, which contains 0.2 mol of NaOH and dilute the solution with water to 1 litre. Now, how much volume of concentrated (1M) NaOH solution be taken, which contains 0.2 moles of NaOH can be calculated as follows: If 1 mol is present in 1L or 1000 mL solution then, 0.2 mol is present in 1000 1 0 2 mL mol × . mol solution = 200 mL solution Thus, 200 mL of 1M NaOH are taken and enough water is added to dilute it to make it 1 litre. In fact for such calculations, a general formula, M1×V1 = M2× V2 where M and V are molarity and volume, respectively, can be used. In this case, M1 is equal to 0.2M; V1 = 1000 mL and, M2 = 1.0M; V2 is to be calculated. Substituting the values in the formula: 0.2 M × 1000 mL = 1.0 M × V2 Note that the number of moles of solute (NaOH) was 0.2 in 200 mL and it has remained the same, i.e., 0.2 even after dilution ( in 1000 mL) as we have changed just the amount of solvent (i.e., water) and have not done anything with respect to NaOH. But keep in mind the concentration. 1. Mass per cent It is obtained by using the following relation: Problem 1.6 A solution is prepared by adding 2 g of a substance A to 18 g of water. Calculate the mass per cent of the solute. Solution 2. Mole Fraction It is the ratio of number of moles of a particular component to the total number of moles of the solution. If a substance 'A' dissolves in substance 'B' and their number of moles are $n_A$ and $n_B$, respectively, then the mole fractions of A and B are given as: = $3.30 \times 10^3$×17 g $NH_3$ (g) = $56.1 \times 10^3$ g $NH_3$ = 56.1 kg $NH_3$ 24 chemistry Summary Chemistry, as we understand it today is not a very old discipline. People in ancient India, already had the

knowledge of many scientific phenomenon much before the advent of modern science. They applied the knowledge in various walks of life. The study of chemistry is very important as its domain encompasses every sphere of life. Chemists study the properties and structure of substances and the changes undergone by them. All substances contain matter, which can exist in three states – solid, liquid or gas. The constituent particles are held in different ways in these states of matter and they exhibit their characteristic properties. Matter can also be classified into elements, compounds or mixtures. An element contains particles of only one type, which may be atoms or molecules. The compounds are formed where atoms of two or more elements combine in a fixed ratio to each other. Mixtures occur widely and many of the substances present around us are mixtures. When the properties of a substance are studied, measurement is inherent. The quantification of properties requires a system of measurement and units in which the quantities are to be expressed. Many systems of measurement exist, of which the English Problem 1.8 The density of 3 M solution of NaCl is 1.25 g mL–1. Calculate the molality of the solution. Solution M = 3 mol L–1 Mass of NaCl in 1 L solution = 3 × 58.5 = 175.5 g Mass of 1L solution = 1000 × 1.25 = 1250 g (since density = 1.25 g mL–1) Mass of water in solution = 1250 –75.5 = 1074.5 g Molality = No. of moles of solute Mass of solvent in kg = 3 mol 1. k 0745 g = 2.79 m Often in a chemistry laboratory, a solution of a desired concentration is prepared by diluting a solution of known higher concentration. The solution of higher concentration is also known as stock solution. Note that the molality of a solution does not change with temperature since mass remains unaffected with temperature. Problem 1.7 Calculate the molarity of NaOH in the solution prepared by dissolving its 4 g in enough water to form 250 mL of the solution. Solution Since molarity (M) Note that molarity of a solution depends upon temperature because volume of a solution is temperature dependent. 4. Molality It is defined as the number of moles of solute present in 1 kg of solvent. It is denoted by m. Thus, Molality (m) = No. of moles of solute Mass of solvent in kg Rationalised 2023-24 Some Basic Concepts of Chemistry 25 and the Metric Systems are widely used. The scientific community, however, has agreed to have a uniform and common system throughout the world, which is abbreviated as SI units (International System of Units). Since measurements involve recording of data, which are always associated with a certain amount of uncertainty, the proper handling of data obtained by measuring the quantities is very important. The measurements of quantities in chemistry are spread over a wide range of 10–31 to 10+23. Hence, a convenient system of expressing the numbers in scientific notation is used. The uncertainty is taken care of by specifying the number of significant figures, in which the observations are reported. The dimensional analysis helps to express the measured quantities in different systems of units. Hence, it is possible to interconvert the results from one system of units to another. The combination of different atoms is governed by basic laws of chemical combination — these being the Law of Conservation of Mass, Law of Definite Proportions, Law of Multiple Proportions, Gay Lussac's Law of Gaseous Volumes and Avogadro Law. All these laws led to the Dalton's atomic theory, which states that atoms are building blocks of matter. The atomic mass of an element is expressed relative to 12C isotope of carbon, which has an exact value of 12u. Usually, the atomic mass used for an element is the average atomic mass obtained by taking into account the natural abundance of different isotopes of that element. The molecular mass of a molecule is obtained by taking sum of the atomic masses of different atoms present in a molecule. The molecular formula can be calculated by determining the mass per cent of different elements present in a compound and its molecular mass. The number of atoms, molecules or any other particles present in a given system are expressed in the terms of Avogadro constant (6.022 × 1023). This is known as 1 mol of the respective particles or entities. Chemical reactions represent the chemical changes undergone by different elements and compounds. A balanced chemical equation provides a lot of information. The coefficients indicate the molar ratios and the respective number of particles taking part in a particular reaction. The quantitative study of the reactants required or the products formed is called

stoichiometry. Using stoichiometric calculations, the amount of one or more reactant(s) required to produce a particular amount of product can be determined and vice-versa. The amount of substance present in a given volume of a solution is expressed in number of ways, e.g., mass per cent, mole fraction, molarity and molality.

**exerciseS** 1.1 Calculate the molar mass of the following: (i) $H_2O$ (ii) $CO_2$ (iii) $CH_4$ 1.2 Calculate the mass per cent of different elements present in sodium sulphate ($Na_2SO_4$). 1.3 Determine the empirical formula of an oxide of iron, which has 69.9% iron and 30.1% dioxygen by mass. 1.4 Calculate the amount of carbon dioxide that could be produced when (i) 1 mole of carbon is burnt in air. (ii) 1 mole of carbon is burnt in 16 g of dioxygen. (iii) 2 moles of carbon are burnt in 16 g of dioxygen. 1.5 Calculate the mass of sodium acetate ($CH_3COONa$) required to make 500 mL of 0.375 molar aqueous solution. Molar mass of sodium acetate is 82.0245 g mol–1. Rationalised 2023-24 26 chemistry 1.6 Calculate the concentration of nitric acid in moles per litre in a sample which has a density, 1.41 g mL–1 and the mass per cent of nitric acid in it being 69%. 1.7 How much copper can be obtained from 100 g of copper sulphate ($CuSO_4$)? 1.8 Determine the molecular formula of an oxide of iron, in which the mass per cent of iron and oxygen are 69.9 and 30.1, respectively. 1.9 Calculate the atomic mass (average) of chlorine using the following data: % Natural Abundance Molar Mass 35Cl 75.77 34.9689 37Cl 24.23 36.9659 1.10 In three moles of ethane ($C_2H_6$), calculate the following: (i) Number of moles of carbon atoms. (ii) Number of moles of hydrogen atoms. (iii) Number of molecules of ethane. 1.11 What is the concentration of sugar ($C_{12}H_{22}O_{11}$) in mol L–1 if its 20 g are dissolved in enough water to make a final volume up to 2L? 1.12 If the density of methanol is 0.793 kg L–1, what is its volume needed for making 2.5 L of its 0.25 M solution? 1.13 Pressure is determined as force per unit area of the surface. The SI unit of pressure, pascal is as shown below: $1Pa = 1N$ m–2 If mass of air at sea level is 1034 g cm–2, calculate the pressure in pascal. 1.14 What is the SI unit of mass? How is it defined? 1.15 Match the following prefixes with their multiples: Prefixes Multiples (i) micro 106 (ii) deca 109 (iii) mega 10–6 (iv) giga 10–15 (v) femto 10 1.16 What do you mean by significant figures? 1.17 A sample of drinking water was found to be severely contaminated with chloroform, $CHCl_3$, supposed to be carcinogenic in nature. The level of contamination was 15 ppm (by mass). (i) Express this in per cent by mass. (ii) Determine the molality of chloroform in the water sample. 1.18 Express the following in the scientific notation: (i) 0.0048 (ii) 234,000 (iii) 8008 (iv) 500.0 (v) 6.0012 1.19 How many significant figures are present in the following? (i) 0.0025 (ii) 208 (iii) 5005 Rationalised 2023-24 Some Basic Concepts of Chemistry 27 (iv) 126,000 (v) 500.0 (vi) 2.0034 1.20 Round up the following upto three significant figures: (i) 34.216 (ii) 10.4107 (iii) 0.04597 (iv) 2808 1.21 The following data are obtained when dinitrogen and dioxygen react together to form different compounds: Mass of dinitrogen Mass of dioxygen (i) 14 g 16 g (ii) 14 g 32 g (iii) 28 g 32 g (iv) 28 g 80 g (a) Which law of chemical combination is obeyed by the above experimental data? Give its statement. (b) Fill in the blanks in the following conversions: (i) 1 km = ...................... mm = ...................... pm (ii) 1 mg = ...................... kg = ...................... ng (iii) 1 mL = ...................... L = ...................... dm3 1.22 If the speed of light is $3.0 \times 10^8$ m s–1, calculate the distance covered by light in 2.00 ns. 1.23 In a reaction $A + B_2 \delta AB_2$ Identify the limiting reagent, if any, in the following reaction mixtures. (i) 300 atoms of A + 200 molecules of B (ii) 2 mol A + 3 mol B (iii) 100 atoms of A + 100 molecules of B (iv) 5 mol A + 2.5 mol B (v) 2.5 mol A + 5 mol B 1.24 Dinitrogen and dihydrogen react with each other to produce ammonia according to the following chemical equation: $N_2$ (g) + $H_2$ (g) $\delta$ $2NH_3$ (g) (i) Calculate the mass of ammonia produced if $2.00 \times 10^3$ g dinitrogen reacts with $1.00 \times 10^3$ g of dihydrogen. (ii) Will any of the two reactants remain unreacted? (iii) If yes, which one and what would be its mass? 1.25 How are 0.50 mol $Na_2CO_3$ and 0.50 M $Na_2CO_3$ different? 1.26 If 10 volumes of dihydrogen gas reacts with five volumes of dioxygen gas, how many volumes of water vapour would be produced? 1.27 Convert the following into basic units: (i) 28.7 pm (ii) 15.15 pm (iii) 25365 mg Rationalised 2023-24 28 chemistry 1.28 Which one of the following will have the largest number of atoms? (i) 1 g Au (s) (ii) 1 g Na (s) (iii) 1 g Li (s) (iv) 1 g of

Cl2(g) 1.29 Calculate the molarity of a solution of ethanol in water, in which the mole fraction of ethanol is 0.040 (assume the density of water to be one). 1.30 What will be the mass of one 12C atom in g? 1.31 How many significant figures should be present in the answer of the following calculations? (i) $\frac{0.02856 \times 298.15 \times 0.112}{0.5785}$ (ii) 5 × 5.364 (iii) 0.0125 + 0.7864 + 0.0215 1.32 Use the data given in the following table to calculate the molar mass of naturally occuring argon isotopes: Isotope Isotopic molar mass Abundance 36Ar 35.96755 g mol–1 0.337% 38Ar 37.96272 g mol–1 0.063% 40Ar 39.9624 g mol–1 99.600% 1.33 Calculate the number of atoms in each of the following (i) 52 moles of Ar (ii) 52 u of He (iii) 52 g of He. 1.34 A welding fuel gas contains carbon and hydrogen only. Burning a small sample of it in oxygen gives 3.38 g carbon dioxide, 0.690 g of water and no other products. A volume of 10.0 L (measured at STP) of this welding gas is found to weigh 11.6 g. Calculate (i) empirical formula, (ii) molar mass of the gas, and (iii) molecular formula. 1.35 Calcium carbonate reacts with aqueous HCl to give CaCl2 and CO2 according to the reaction, CaCO3 (s) + 2 HCl (aq) → CaCl2 (aq) + CO2(g) + H2O(l) What mass of CaCO3 is required to react completely with 25 mL of 0.75 M HCl? 1.36 Chlorine is prepared in the laboratory by treating manganese dioxide (MnO2) with aqueous hydrochloric acid according to the reaction 4 HCl (aq) + MnO2(s) → 2H2O (l) + MnCl2(aq) + Cl2 (g) How many grams of HCl react with 5.0 g of manganese dioxide? Rationalised 2023-24The rich diversity of chemical behaviour of different elements can be traced to the differences in the internal structure of atoms of these elements. Unit 2 structure of atom After studying this unit you will be able to • know about the discovery of electron, proton and neutron and their characteristics; • describe Thomson, Rutherford and Bohr atomic models; • understand the important features of the quantum mechanical model of atom; • understand nat u r e o f electromagnetic radiation and Planck's quantum theory; • explain the photoelectric effect and describe features of atomic spectra; • state the de Broglie relation and Heisenberg uncertainty principle; • define an atomic orbital in terms of quantum numbers; • state aufbau principle, Pauli exclusion principle and Hund's rule of maximum multiplicity; and • write the electronic configurations of atoms. The existence of atoms has been proposed since the time of early Indian and Greek philosophers (400 B.C.) who were of the view that atoms are the fundamental building blocks of matter. According to them, the continued subdivisions of matter would ultimately yield atoms which would not be further divisible. The word 'atom' has been derived from the Greek word 'a-tomio' which means 'uncut-able' or 'non-divisible'. These earlier ideas were mere speculations and there was no way to test them experimentally. These ideas remained dormant for a very long time and were revived again by scientists in the nineteenth century. The atomic theory of matter was first proposed on a firm scientific basis by John Dalton, a British school teacher in 1808. His theory, called Dalton's atomic theory, regarded the atom as the ultimate particle of matter (Unit 1). Dalton's atomic theory was able to explain the law of conservation of mass, law of constant composition and law of multiple proportion very successfully. However, it failed to explain the results of many experiments, for example, it was known that substances like glass or ebonite when rubbed with silk or fur get electrically charged. In this unit we start with the experimental observations made by scientists towards the end of nineteenth and beginning of twentieth century. These established that atoms are made of sub-atomic particles, i.e., electrons, protons and neutrons — a concept very different from that of Dalton. Objectives Rationalised 2023-24 30 chemistry 2.1 Discovery of Sub-atomic Particles An insight into the structure of atom was obtained from the experiments on electrical discharge through gases. Before we discuss these results we need to keep in mind a basic rule regarding the behaviour of charged particles : "Like charges repel each other and unlike charges attract each other". 2.1.1 Discovery of Electron In 1830, Michael Faraday showed that if electricity is passed through a solution of an electrolyte, chemical reactions occurred at the electrodes, which resulted in the liberation and deposition of matter at the electrodes. He formulated certain laws which you will study in Class XII. These results suggested the particulate nature of electricity. In mid 1850s many

scientists mainly Faraday began to study electrical discharge in partially evacuated tubes, known as cathode ray discharge tubes. It is depicted in Fig. 2.1. A cathode ray tube is made of glass containing two thin pieces of metal, called electrodes, sealed in it. The electrical discharge through the gases could be observed only at very low pressures and at very high voltages. The pressure of different gases could be adjusted by evacuation of the glass tubes. When sufficiently high voltage is applied across the electrodes, current starts flowing through a stream of particles moving in the tube from the negative electrode (cathode) to the positive electrode (anode). These were called cathode rays or cathode ray particles. The flow of current from cathode to anode was further checked by making a hole in the anode and coating the tube behind anode with phosphorescent material zinc sulphide. When these rays, after passing through anode, strike the zinc sulphide coating, a bright spot is developed on the coating [Fig. 2.1(b)]. Fig. 2.1(a) A cathode ray discharge tube Fig. 2.1(b) A cathode ray discharge tube with perforated anode The results of these experiments are summarised below. (i) The cathode rays start from cathode and move towards the anode. (ii) These rays themselves are not visible but their behaviour can be observed with the help of certain kind of materials (fluorescent or phosphorescent) which glow when hit by them. Television picture tubes are cathode ray tubes and television pictures result due to fluorescence on the television screen coated with certain fluorescent or phosphorescent materials. (iii) In the absence of electrical or magnetic field, these rays travel in straight lines (Fig. 2.2). (iv) In the presence of electrical or magnetic field, the behaviour of cathode rays are similar to that expected from negatively charged particles, suggesting that the cathode rays consist of negatively charged particles, called electrons. (v) The characteristics of cathode rays (electrons) do not depend upon the Rationalised 2023-24 structure of atom 31 material of electrodes and the nature of the gas present in the cathode ray tube. Thus, we can conclude that electrons are basic constituent of all the atoms. 2.1.2 Charge to Mass Ratio of Electron In 1897, British physicist J.J. Thomson measured the ratio of electrical charge (e) to the mass of electron ($m_e$ ) by using cathode ray tube and applying electrical and magnetic field perpendicular to each other as well as to the path of electrons (Fig. 2.2). When only electric field is applied, the electrons deviate from their path and hit the cathode ray tube at point A (Fig. 2.2). Similarly when only magnetic field is applied, electron strikes the cathode ray tube at point C. By carefully balancing the electrical and magnetic field strength, it is possible to bring back the electron to the path which is followed in the absence of electric or magnetic field and they hit the screen at point B. Thomson argued that the amount of deviation of the particles from their path in the presence of electrical or magnetic field depends upon: (i) the magnitude of the negative charge on the particle, greater the magnitude of the charge on the particle, greater is the interaction with the electric or magnetic field and thus greater is the deflection. (ii) the mass of the particle — lighter the particle, greater the deflection. (iii) the strength of the electrical or magnetic field — the deflection of electrons from its original path increases with the increase in the voltage across the electrodes, or the strength of the magnetic field. By carrying out accurate measurements on the amount of deflections observed by the electrons on the electric field strength or magnetic field strength, Thomson was able to determine the value of $e/m_e$ as: = $1.758820 \times 10^{11}$ C kg$^{-1}$ (2.1) Where $m_e$ is the mass of the electron in kg and e is the magnitude of the charge on the electron in coulomb (C). Since electrons are negatively charged, the charge on electron is –e. 2.1.3 Charge on the Electron R.A. Millikan (1868-1953) devised a method known as oil drop experiment (1906-14), to determine the charge on the electrons. He found the charge on the electron to be – $1.6 \times 10^{-19}$ C. The present accepted value of electrical charge is – $1.602176 \times 10^{-19}$ C. The mass of the electron ($m_e$ ) was determined by combining these results with Thomson's value of $e/m_e$ ratio. = $9.1094 \times 10^{-31}$ kg (2.2) Fig. 2.2 The apparatus to determine the charge to the mass ratio of electron Rationalised 2023-24 32 chemistry 2.1.4 Discovery of Protons and Neutrons Electrical discharge carried out in the modified cathode ray tube led to the discovery of canal rays carrying positively charged particles. The characteristics of these positively charged particles are

listed below. (i) Unlike cathode rays, mass of positively charged particles depends upon the nature of gas present in the cathode ray tube. These are simply the positively charged gaseous ions. (ii) The charge to mass ratio of the particles depends on the gas from which these originate. (iii) Some of the positively charged particles carry a multiple of the fundamental unit of electrical charge. (iv) The behaviour of these particles in the magnetic or electrical field is opposite to that observed for electron or cathode rays. The smallest and lightest positive ion was obtained from hydrogen and was called proton. This positively charged particle was characterised in 1919. Later, a need was felt for the presence of electrically neutral particle as one of the constituent of atom. These particles were discovered by Chadwick (1932) by bombarding a thin sheet of beryllium by α-particles. When electrically neutral particles having a mass slightly greater than that of protons were emitted. He named these particles as neutrons. The important properties of all these fundamental particles are given in Table 2.1. 2.2 Atomic Models Observations obtained from the experiments mentioned in the previous sections have suggested that Dalton's indivisible atom is composed of sub-atomic particles carrying positive and negative charges. The major problems before the scientists after the discovery of sub-atomic particles were: • to account for the stability of atom, • to compare the behaviour of elements in terms of both physical and chemical properties, Millikan's Oil Drop Method In this method, oil droplets in the form of mist, produced by the atomiser, were allowed to enter through a tiny hole in the upper plate of electrical condenser. The downward motion of these droplets was viewed through the telescope, equipped with a micrometer eye piece. By measuring the rate of fall of these droplets, Millikan was able to measure the mass of oil droplets. The air inside the chamber was ionized by passing a beam of X-rays through it. The electrical charge on these oil droplets was acquired by collisions with gaseous ions. The fall of these charged oil droplets can be retarded, accelerated or made stationary depending upon the charge on the droplets and the polarity and strength of the voltage applied to the plate. By carefully measuring the effects of electrical field strength on the motion of oil droplets, Millikan concluded that the magnitude of electrical charge, q, on the droplets is always an integral multiple of the electrical charge, e, that is, q = n e, where n = 1, 2, 3... . • to explain the formation of different kinds of molecules by the combination of different atoms and, • to understand the origin and nature of the characteristics of electromagnetic radiation absorbed or emitted by atoms. Fig. 2.3 The Millikan oil drop apparatus for measuring charge 'e'. In chamber, the forces acting on oil drop are: gravitational, electrostatic due to electrical field and a viscous drag force when the oil drop is moving. Rationalised 2023-24 structure of atom 33 Different atomic models were proposed to explain the distributions of these charged particles in an atom. Although some of these models were not able to explain the stability of atoms, two of these models, one proposed by J.J. Thomson and the other proposed by Ernest Rutherford are discussed below. 2.2.1 Thomson Model of Atom J. J. Thomson, in 1898, proposed that an atom possesses a spherical shape (radius approximately 10–10 m) in which the positive charge is uniformly distributed. The electrons are embedded into it in such a manner as to give the most stable electrostatic arrangement (Fig. 2.4). Many different names are given to this model, for example, plum pudding, raisin pudding or watermelon. This model In the later half of the nineteenth century different kinds of rays were discovered, besides those mentioned earlier. Wilhalm Röentgen (1845-1923) in 1895 showed that when electrons strike a material in the cathode ray tubes, produce rays which can cause fluorescence in the fluorescent materials placed outside the cathode ray tubes. Since Röentgen did not know the nature of the radiation, he named them X-rays and the name is still carried on. It was noticed that X-rays are produced effectively when electrons strike the dense metal anode, called targets. These are not deflected by the electric and magnetic fields and have a very high penetrating power through the matter and that is the reason that these rays are used to study the interior of the objects. These rays are of very short wavelengths (~0.1 nm) and possess electro-magnetic character (Section 2.3.1). Henri Becqueral (1852-1908) observed that there are certain elements which emit radiation on their

own and named this phenomenon as radioactivity and the elements known as radioactive elements. This field was developed by Marie Curie, Piere Curie, Rutherford and Fredrick Soddy. It was observed that three kinds of rays i.e., α, β- and γ-rays are emitted. Rutherford found that α-rays consists of high energy particles carrying two units of positive charge and four unit of atomic mass. He concluded that α- particles are helium nuclei as when αparticles combined with two electrons yielded helium gas. β-rays are negatively charged Fig.2.4 Thomson model of atom can be visualised as a pudding or watermelon of positive charge with plums or seeds (electrons) embedded into it. An important feature of this model is that the mass of the atom is assumed to be uniformly distributed over the atom. Although this model was able to explain the overall neutrality of the atom, but was not consistent with the results of later experiments. Thomson was awarded Nobel Prize for physics in 1906, for his theoretical and experimental investigations on the conduction of electricity by gases. Table 2.1 Properties of Fundamental Particles Name Symbol Absolute charge/C Relative charge Mass/kg Mass/u Approx. mass/u Electron Proton Neutron e p n – 1.602176×10–19 + 1.602176×10–19 0 –1 +1 0 9.109382×10–31 1.6726216×10–27 1.674927×10–27 0.00054 1.00727 1.00867 0 1 1 Rationalised 2023-24 34 chemistry represented in Fig. 2.5. A stream of high energy α–particles from a radioactive source was directed at a thin foil (thickness ∼ 100 nm) of gold metal. The thin gold foil had a circular fluorescent zinc sulphide screen around it. Whenever α–particles struck the screen, a tiny flash of light was produced at that point. The results of scattering experiment were quite unexpected. According to Thomson model of atom, the mass of each gold atom in the foil should have been spread evenly over the entire atom, and α–particles had enough energy to pass directly through such a uniform distribution of mass. It was expected that the particles would slow down and change directions only by a small angles as they passed through the foil. It was observed that: (i) most of the α–particles passed through the gold foil undeflected. (ii) a small fraction of the α–particles was deflected by small angles. (iii) a very few α–particles (∼1 in 20,000) bounced back, that is, were deflected by nearly 180° . On the basis of the observations, Rutherford drew the following conclusions regarding the structure of atom: (i) Most of the space in the atom is empty as most of the α–particles passed through the foil undeflected. (ii) A few positively charged α–particles were deflected. The deflection must be due to enormous repulsive force showing that the positive charge of the atom is not spread throughout the atom as Thomson had presumed. The positive charge has to be concentrated in a very small volume that repelled and deflected the positively charged α–particles. (iii) Calculations by Rutherford showed that the volume occupied by the nucleus is negligibly small as compared to the total volume of the atom. The radius of the atom is about 10–10 m, while that of nucleus is 10–15 m. One can appreciate this difference in size by realising that if Fig. 2.5 Schematic view of Rutherford's scattering experiment. When a beam of alpha (▢) particles is "shot" at a thin gold foil, most of them pass through without much effect. Some, however, are deflected. A. Rutherford's scattering experiment B. Schematic molecular view of the gold foil 2.2.2 Rutherford's Nuclear Model of Atom Rutherford and his students (Hans Geiger and Ernest Marsden) bombarded very thin gold foil with α–particles. Rutherford's famous –particle scattering experiment is particles similar to electrons. The γ-rays are high energy radiations like X-rays, are neutral in nature and do not consist of particles. As regards penetrating power, α-particles are the least, followed by β-rays (100 times that of α–particles) and γ-rays (1000 times of that α-particles). Rationalised 2023-24 structure of atom 35 a cricket ball represents a nucleus, then the radius of atom would be about 5 km. On the basis of above observations and conclusions, Rutherford proposed the nuclear model of atom. According to this model: (i) The positive charge and most of the mass of the atom was densely concentrated in extremely small region. This very small portion of the atom was called nucleus by Rutherford. (ii) The nucleus is surrounded by electrons that move around the nucleus with a very high speed in circular paths called orbits. Thus, Rutherford's model of atom resembles the solar system in which the nucleus plays the role of sun and the electrons that of revolving planets. (iii)

Electrons and the nucleus are held together by electrostatic forces of attraction. 2.2.3 Atomic Number and Mass Number The presence of positive charge on the nucleus is due to the protons in the nucleus. As established earlier, the charge on the proton is equal but opposite to that of electron. The number of protons present in the nucleus is equal to atomic number (Z ). For example, the number of protons in the hydrogen nucleus is 1, in sodium atom it is 11, therefore their atomic numbers are 1 and 11 respectively. In order to keep the electrical neutrality, the number of electrons in an atom is equal to the number of protons (atomic number, Z ). For example, number of electrons in hydrogen atom and sodium atom are 1 and 11 respectively. Atomic number (Z) = number of protons in the nucleus of an atom = number of electrons in a nuetral atom (2.3) While the positive charge of the nucleus is due to protons, the mass of the nucleus, due to protons and neutrons. As discussed earlier protons and neutrons present in the nucleus are collectively known as nucleons. The total number of nucleons is termed as mass number (A) of the atom. mass number (A) = number of protons (Z ) + number of neutrons (n) (2.4) 2.2.4 Isobars and Isotopes The composition of any atom can be represented by using the normal element symbol (X) with super-script on the left hand side as the atomic mass number (A) and subscript (Z) on the left hand side as the atomic number (i.e., A Z X). Isobars are the atoms with same mass number but different atomic number for example, 6 14C and 7 14N. On the other hand, atoms with identical atomic number but different atomic mass number are known as Isotopes. In other words (according to equation 2.4), it is evident that difference between the isotopes is due to the presence of different number of neutrons present in the nucleus. For example, considering of hydrogen atom again, 99.985% of hydrogen atoms contain only one proton. This isotope is called protium (1 1H). Rest of the percentage of hydrogen atom contains two other isotopes, the one containing 1 proton and 1 neutron is called deuterium ( 1 2D, 0.015%) and the other one possessing 1 proton and 2 neutrons is called tritium ( 1 3T ). The latter isotope is found in trace amounts on the earth. Other examples of commonly occuring isotopes are: carbon atoms containing 6, 7 and 8 neutrons besides 6 protons ( 6 12 6 13 6 14 C, C, C ); chlorine atoms containing 18 and 20 neutrons besides 17 protons ( 17 35 17 37 Cl, Cl ). Lastly an important point to mention regarding isotopes is that chemical properties of atoms are controlled by the number of electrons, which are determined by the number of protons in the nucleus. Number of neutrons present in the nucleus have very little effect on the chemical properties of an element. Therefore, all the isotopes of a given element show same chemical behaviour. Rationalised 2023-24 36 chemistry Problem 2.1 Calculate the number of protons, neutrons and electrons in 80 35Br . Solution In this case, 80 35Br , Z = 35, A = 80, species is neutral Number of protons = number of electrons = Z = 35 Number of neutrons = 80 − 35 = 45, (equation 2.4) Problem 2.2 The number of electrons, protons and neutrons in a species are equal to 18, 16 and 16 respectively. Assign the proper symbol to the species. Solution The atomic number is equal to number of protons = 16. The element is sulphur (S). Atomic mass number = number of protons + number of neutrons = 16 + 16 = 32 Species is not neutral as the number of protons is not equal to electrons. It is anion (negatively charged) with charge equal to excess electrons = 18 − 16 = 2. Symbol is . Note : Before using the notation A Z X, find out whether the species is a neutral atom, a cation or an anion. If it is a neutral atom, equation (2.3) is valid, i.e., number of protons = number of electrons = atomic number. If the species is an ion, determine whether the number of protons are larger (cation, positive ion) or smaller (anion, negative ion) than the number of electrons. Number of neutrons is always given by A–Z, whether the species is neutral or ion. 2.2.5 Drawbacks of Rutherford Model As you have learnt above, Rutherford nuclear model of an atom is like a small scale solar system with the nucleus playing the role * Classical mechanics is a theoretical science based on Newton's laws of motion. It specifies the laws of motion of macroscopic objects. of the massive sun and the electrons being similar to the lighter planets. When classical mechanics* is applied to the solar system, it shows that the planets describe well-defined orbits around the sun. The gravitational force between the planets

is given by the expression G. 1 2 2 m m r - ▢▢▢▢ where m1 and m2 are the masses, r is the distance of separation of the masses and G is the gravitational constant. The theory can also calculate precisely the planetary orbits and these are in agreement with the experimental measurements. The similarity between the solar system and nuclear model suggests that electrons should move around the nucleus in well defined orbits. Further, the coulomb force (kq1q2/r2 where q1 and q2 are the charges, r is the distance of separation of the charges and k is the proportionality constant) between electron and the nucleus is mathematically similar to the gravitational force. However, when a body is moving in an orbit, it undergoes acceleration even if it is moving with a constant speed in an orbit because of changing direction. So an electron in the nuclear model describing planet like orbits is under acceleration. According to the electromagnetic theory of Maxwell, charged particles when accelerated should emit electromagnetic radiation (This feature does not exist for planets since they are uncharged). Therefore, an electron in an orbit will emit radiation, the energy carried by radiation comes from electronic motion. The orbit will thus continue to shrink. Calculations show that it should take an electron only 10–8 s to spiral into the nucleus. But this does not happen. Thus, the Rutherford model cannot explain the stability of an atom. If the motion of an electron is described on the basis of the classical mechanics and electromagnetic theory, you may ask that since the motion of electrons in orbits is leading to the instability of the atom, then why not consider electrons as stationary Rationalised 2023-24 structure of atom 37 around the nucleus. If the electrons were stationary, electrostatic attraction between the dense nucleus and the electrons would pull the electrons toward the nucleus to form a miniature version of Thomson's model of atom. Another serious drawback of the Rutherford model is that it says nothing about distribution of the electrons around the nucleus and the energies of these electrons. 2.3 Developments Leading to the Bohr's Model of Atom Historically, results observed from the studies of interactions of radiations with matter have provided immense information regarding the structure of atoms and molecules. Neils Bohr utilised these results to improve upon the model proposed by Rutherford. Two developments played a major role in the formulation of Bohr's model of atom. These were: (i) Dual character of the electromagnetic radiation which means that radiations possess both wave like and particle like properties, and (ii) Experimental results regarding atomic spectra. First, we will discuss about the duel nature of electromagnetic radiations. Experimental results regarding atomic spectra will be discussed in Section 2.4. 2.3.1 Wave Nature of Electromagnetic Radiation In the mid-nineteenth century, physicists actively studied absorption and emission of radiation by heated objects. These are called thermal radiations. They tried to find out of what the thermal radiation is made. It is now a well-known fact that thermal radiations consist of electromagnetic waves of various frequencies or wavelengths. It is based on a number of modern concepts, which were unknown in the mid-nineteenth century. First active study of thermal radiation laws occured in the 1850's and the theory of electromagnetic waves and the emission of such waves by accelerating charged particles was developed in the early 1870's by James Clerk Maxwell, which was experimentally confirmed later by Heinrich Hertz. Here, we will learn some facts about electromagnetic radiations. James Maxwell (1870) was the first to give a comprehensive explanation about the interaction between the charged bodies and the behaviour of electrical and magnetic fields on macroscopic level. He suggested that when electrically charged particle moves under accelaration, alternating electrical and magnetic fields are produced and transmitted. These fields are transmitted in the forms of waves called electromagnetic waves or electromagnetic radiation. Light is the form of radiation known from early days and speculation about its nature dates back to remote ancient times. In earlier days (Newton) light was supposed to be made of particles (corpuscles). It was only in the 19th century when wave nature of light was established. Maxwell was again the first to reveal that light waves are associated with oscillating electric and magnetic character (Fig. 2.6). Although electromagnetic wave motion is complex in nature, we will consider here only a few simple properties. (i) The oscillating electric and

magnetic fields produced by oscillating charged Fig.2.6 The electric and magnetic field components of an electromagnetic wave. These components have the same wavelength, frequency, speed and amplitude, but they vibrate in two mutually perpendicular planes. Rationalised 2023-24 38 chemistry particles are perpendicular to each other and both are perpendicular to the direction of propagation of the wave. Simplified picture of electromagnetic wave is shown in Fig. 2.6. (ii) Unlike sound waves or waves produced in water, electromagnetic waves do not require medium and can move in vacuum. (iii) It is now well established that there are many types of electromagnetic radiations, which differ from one another in wavelength (or frequency). These constitute what is called electromagnetic spectrum (Fig. 2.7). Different regions of the spectrum are identified by different names. Some examples are: radio frequency region around $10^6$ Hz, used for broadcasting; microwave region around $10^{10}$ Hz used for radar; infrared region around $10^{13}$ Hz used for heating; ultraviolet region around $10^{16}$Hz a component of sun's radiation. The small portion around $10^{15}$ Hz, is what is ordinarily called visible light. It is only this part which our eyes can see (or detect). Special instruments are required to detect non-visible radiation. (iv) Different kinds of units are used to represent electromagnetic radiation. These radiations are characterised by the properties, namely, frequency ($\nu$) and wavelength ($\lambda$). The SI unit for frequency ($\nu$) is hertz (Hz, $s^{-1}$), after Heinrich Hertz. It is defined as the number of waves that pass a given point in one second. Wavelength should have the units of length and as you know that the SI units of length is meter (m). Since electromagnetic radiation consists of different kinds of waves of much smaller wavelengths, smaller units are used. Fig. 2.7 shows various types of electro-magnetic radiations which differ from one another in wavelengths and frequencies. In vaccum all types of electromagnetic radiations, regardless of wavelength, travel at the same speed, i.e., $3.0 × 10^8$ m $s^{-1}$ ($2.997925 × 10^8$ $ms^{-1}$, to be precise). This is called speed of light and is given the symbol 'c'. The frequency ($\nu$ ), wavelength ($\lambda$) and velocity of light (c) are related by the equation (2.5). c = $\nu$ $\lambda$ (2.5) Fig. 2.7 (a) The spectrum of electromagnetic radiation. (b) Visible spectrum. The visible region is only a small part of the entire spectrum. (a) (b) Rationalised 2023-24 structure of atom 39 The other commonly used quantity specially in spectroscopy, is the wavenumber ( ). It is defined as the number of wavelengths per unit length. Its units are reciprocal of wavelength unit, i.e., $m^{-1}$. However commonly used unit is $cm^{-1}$ (not SI unit). Problem 2.3 The Vividh Bharati station of All India Radio, Delhi, broadcasts on a frequency of 1,368 kHz (kilo hertz). Calculate the wavelength of the electromagnetic radiation emitted by transmitter. Which part of the electromagnetic spectrum does it belong to? Solution The wavelength, $\lambda$, is equal to c/$\nu$, where c is the speed of electromagnetic radiation in vacuum and $\nu$ is the frequency. Substituting the given values, we have  - c $\nu$ This is a characteristic radiowave wavelength. Problem 2.4 The wavelength range of the visible spectrum extends from violet (400 nm) to red (750 nm). Express these wavelengths in frequencies (Hz). (1nm = $10^{-9}$ m) Solution Using equation 2.5, frequency of violet light = $7.50 × 10^{14}$ Hz * Diffraction is the bending of wave around an obstacle. ** Interference is the combination of two waves of the same or different frequencies to give a wave whose distribution at each point in space is the algebraic or vector sum of disturbances at that point resulting from each interfering wave. Frequency of red light $\nu$ = = $4.00 × 10^{14}$ Hz The range of visible spectrum is from $4.0 × 10^{14}$ to $7.5 × 10^{14}$ Hz in terms of frequency units. Problem 2.5 Calculate (a) wavenumber and (b) frequency of yellow radiation having wavelength 5800 Å. Solution (a) Calculation of wavenumber ( ) $\lambda$=5800Å = $5800 × 10^{-8}$ cm = $5800 × 10^{-10}$ m (b) Calculation of the frequency ($\nu$ ) 2.3.2 Particle Nature of Electromagnetic Radiation: Planck's Quantum Theory Some of the experimental phenomenon such as diffraction* and interference** can be explained by the wave nature of the electromagnetic radiation. However, following are some of the observations which could not be explained with the help of even the electromagentic theory of 19th century physics (known as classical physics): (i) the nature of emission of radiation from hot bodies (black-body radiation) (ii) ejection of electrons from metal surface when radiation strikes it (photoelectric effect)

(iii) variation of heat capacity of solids as a function of temperature Rationalised 2023-24 40 chemistry entering the hole will be reflected by the cavity walls and will be eventually absorbed by the walls. A black body is also a perfect radiator of radiant energy. Furthermore, a black body is in thermal equilibrium with its surroundings. It radiates same amount of energy per unit area as it absorbs from its surrounding in any given time. The amount of light emitted (intensity of radiation) from a black body and its spectral distribution depends only on its temperature. At a given temperature, intensity of radiation emitted increases with the increase of wavelength, reaches a maximum value at a given wavelength and then starts decreasing with further increase of wavelength, as shown in Fig. 2.8. Also, as the temperature increases, maxima of the curve shifts to short wavelength. Several attempts were made to predict the intensity of radiation as a function of wavelength. But the results of the above experiment could not be explained satisfactorily on the basis of the wave theory of light. Max Planck arrived at a satisfactory relationship Fig. 2.8(a) Black body Fig. 2.8 Wavelength-intensity relationship (iv) Line spectra of atoms with special reference to hydrogen. These phenomena indicate that the system can take energy only in discrete amounts. All possible energies cannot be taken up or radiated. It is noteworthy that the first concrete explanation for the phenomenon of the black body radiation mentioned above was given by Max Planck in 1900. Let us first try to understand this phenomenon, which is given below: Hot objects emit electromagnetic radiations over a wide range of wavelengths. At high temperatures, an appreciable proportion of radiation is in the visible region of the spectrum. As the temperature is raised, a higher proportion of short wavelength (blue light) is generated. For example, when an iron rod is heated in a furnace, it first turns to dull red and then progressively becomes more and more red as the temperature increases. As this is heated further, the radiation emitted becomes white and then becomes blue as the temperature becomes very high. This means that red radiation is most intense at a particular temperature and the blue radiation is more intense at another temperature. This means intensities of radiations of different wavelengths emitted by hot body depend upon its temperature. By late 1850's it was known that objects made of different material and kept at different temperatures emit different amount of radiation. Also, when the surface of an object is irradiated with light (electromagnetic radiation), a part of radiant energy is generally reflected as such, a part is absorbed and a part of it is transmitted. The reason for incomplete absorption is that ordinary objects are as a rule imperfect absorbers of radiation. An ideal body, which emits and absorbs radiations of all frequencies uniformly, is called a black body and the radiation emitted by such a body is called black body radiation. In practice, no such body exists. Carbon black approximates fairly closely to black body. A good physical approximation to a black body is a cavity with a tiny hole, which has no other opening. Any ray Rationalised 2023-24 structure of atom 41 by making an assumption that absorption and emmission of radiation arises from oscillator i.e., atoms in the wall of black body. Their frequency of oscillation is changed by interaction with oscilators of electromagnetic radiation. Planck assumed that radiation could be sub-divided into discrete chunks of energy. He suggested that atoms and molecules could emit or absorb energy only in discrete quantities and not in a continuous manner. He gave the name quantum to the smallest quantity of energy that can be emitted or absorbed in the form of electromagnetic radiation. The energy (E) of a quantum of radiation is proportional to its frequency (v) and is expressed by equation (2.6). $E = h\upsilon$ (2.6) The proportionality constant, 'h' is known as Planck's constant and has the value $6.626\times10^{-34}$ J s. With this theory, Planck was able to explain the distribution of intensity in the radiation from black body as a function of frequency or wavelength at different temperatures. Quantisation has been compared to standing on a staircase. A person can stand on any step of a staircase, but it is not possible for him/her to stand in between the two steps. The energy can take any one of the values from the following set, but cannot take on any values between them. $E = 0, h\upsilon, 2h\upsilon, 3h\upsilon....nh\upsilon.....$ Photoelectric Effect In 1887, H. Hertz performed a very interesting experiment in which electrons (or

electric current) were ejected when certain metals (for example potassium, rubidium, caesium etc.) were exposed to a beam of light as shown in Fig. 2.9. The phenomenon is called Photoelectric effect. The results observed in this experiment were: (i) The electrons are ejected from the metal surface as soon as the beam of light strikes the surface, i.e., there is no time lag between the striking of light beam and the ejection of electrons from the metal surface. (ii) The number of electrons ejected is proportional to the intensity or brightness of light. (iii) For each metal, there is a characteristic minimum frequency, $v_0$ (also known as threshold frequency) below which photoelectric effect is not observed. At a frequency $v > v_0$, the ejected electrons come out with certain kinetic energy. The kinetic energies of these electrons increase with the increase of frequency of the light used. All the above results could not be explained on the basis of laws of classical physics. According to latter, the energy content of the beam of light depends upon the brightness of the light. In other words, number of electrons ejected and kinetic energy associated with them should depend on the brightness of light. It has been observed that though the number Fig.2.9 Equipment for studying the photoelectric effect. Light of a particular frequency strikes a clean metal surface inside a vacuum chamber. Electrons are ejected from the metal and are counted by a detector that measures their kinetic energy. Max Planck (1858–1947) Max Planck, a German physicist, received his Ph.D in theoretical physics from the University of Munich in 1879. In 1888, he was appointed Director of the Institute of Theoretical Physics at the University of Berlin. Planck was awarded the Nobel Prize in Physics in 1918 for his quantum theory. Planck also made significant contributions in thermodynamics and other areas of physics. Rationalised 2023-24 42 chemistry of electrons ejected does depend upon the brightness of light, the kinetic energy of the ejected electrons does not. For example, red light [$v = (4.3$ to $4.6) \times 10^{14}$ Hz] of any brightness (intensity) may shine on a piece of potassium metal for hours but no photoelectrons are ejected. But, as soon as even a very weak yellow light ($v = 5.1–5.2 \times 10^{14}$ Hz) shines on the potassium metal, the photoelectric effect is observed. The threshold frequency ($v_0$) for potassium metal is $5.0 \times 10^{14}$ Hz. Einstein (1905) was able to explain the photoelectric effect using Planck's quantum theory of electromagnetic radiation as a starting point. the minimum energy required to eject the electron is $hv_0$ (also called work function, $W_0$; Table 2.2), then the difference in energy ($hv – hv_0$ ) is transferred as the kinetic energy of the photoelectron. Following the conservation of energy principle, the kinetic energy of the ejected electron is given by the equation 2.7. (2.7) where $m_e$ is the mass of the electron and $v$ is the velocity associated with the ejected electron. Lastly, a more intense beam of light consists of larger number of photons, consequently the number of electrons ejected is also larger as compared to that in an experiment in which a beam of weaker intensity of light is employed. Dual Behaviour of Electromagnetic Radiation The particle nature of light posed a dilemma for scientists. On the one hand, it could explain the black body radiation and photoelectric effect satisfactorily but on the other hand, it was not consistent with the known wave behaviour of light which could account for the phenomena of interference and diffraction. The only way to resolve the dilemma was to accept the idea that light possesses both particle and wave-like properties, i.e., light has dual behaviour. Depending on the experiment, we find that light behaves either as a wave or as a stream of particles. Whenever radiation interacts with matter, it displays particle like properties in contrast to the wavelike properties (interference and diffraction), which it exhibits when it propagates. This concept was totally alien to the way the scientists thought about matter and radiation and it took them a long time to become convinced of its validity. It turns out, as you shall see later, that some microscopic particles like electrons also exhibit this waveparticle duality. Shining a beam of light on to a metal surface can, therefore, be viewed as shooting a beam of particles, the photons. When a photon of sufficient energy strikes an electron in the atom of the metal, it transfers its energy instantaneously to the electron during the collision and the electron is ejected without any time lag or delay. Greater the energy possessed by the photon, greater will be transfer of energy to the electron and greater

the kinetic energy of the ejected electron. In other words, kinetic energy of the ejected electron is proportional to the frequency of the electromagnetic radiation. Since the striking photon has energy equal to hv and

Table 2.2 Values of Work Function ($W_0$) for a Few Metals

| Metal | Li | Na | K | Mg | Cu | Ag |
|---|---|---|---|---|---|---|
| $W_0$ /eV | 2.42 | 2.3 | 2.25 | 3.7 | 4.8 | 4.3 |

Albert Einstein, a German born American physicist, is regarded by many as one of the two great physicists the world has known (the other is Isaac Newton). His three research papers (on special relativity, Brownian motion and the photoelectric effect) which he published in 1905, while he was employed as a technical assistant in a Swiss patent office in Berne have profoundly influenced the development of physics. He received the Nobel Prize in Physics in 1921 for his explanation of the photoelectric effect.

Albert Einstein (1879–1955)

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**Problem 2.6** Calculate energy of one mole of photons of radiation whose frequency is 5 ×10$^{14}$ Hz.

**Solution** Energy (E) of one photon is given by the expression

E = hv

h = 6.626 ×10$^{–34}$ J s

v = 5×10$^{14}$ s$^{–1}$ (given)

E = (6.626 ×10$^{–34}$ J s) × (5 ×10$^{14}$ s$^{–1}$) = 3.313 ×10$^{–19}$ J

Energy of one mole of photons

= (3.313 ×10$^{–19}$ J) × (6.022 × 10$^{23}$ mol$^{–1}$)

= 199.51 kJ mol$^{–1}$

**Problem 2.7** A 100 watt bulb emits monochromatic light of wavelength 400 nm. Calculate the number of photons emitted per second by the bulb.

**Solution** Power of the bulb = 100 watt = 100 J s$^{–1}$

Energy of one photon E = hv = hc/λ

$= \frac{6.626 \times 10^{-34} J s \times 3 \times 10^{8} m s^{-1}}{400 \times 10^{-9} m}$ = 4.969 × 10$^{–19}$ J

Number of photons emitted $\frac{100 J s^{-1}}{4.969 \times 10^{-19} J} = 2.012 \times 10^{20} s^{-1}$

**Problem 2.8** When electromagnetic radiation of wavelength 300 nm falls on the surface of sodium, electrons are emitted with a kinetic energy of 1.68 ×10$^{5}$ J mol$^{–1}$. What is the minimum energy needed to remove an electron from sodium? What is the maximum wavelength that will cause a photoelectron to be emitted?

**Solution** The energy (E) of a 300 nm photon is given by

= 6.626 × 10$^{–19}$ J

The energy of one mole of photons

= 6.626 ×10$^{–19}$ J × 6.022 × 10$^{23}$ mol$^{–1}$

= 3.99 × 10$^{5}$ J mol$^{–1}$

The minimum energy needed to remove one mole of electrons from sodium

= (3.99 –1.68) 10$^{5}$ J mol$^{–1}$ = 2.31 × 10$^{5}$ J mol$^{–1}$

The minimum energy for one electron

This corresponds to the wavelength

$= \frac{c}{h} = \frac{6.626 \times 10^{-34} J s \times 3.0 \times 10^{8} m s^{-1}}{3.84 \times 10^{-19} J}$

E = 517 nm

(This corresponds to green light)

**Problem 2.9** The threshold frequency v$_0$ for a metal is 7.0 ×10$^{14}$ s$^{–1}$. Calculate the kinetic energy of an electron emitted when radiation of frequency v =1.0 ×10$^{15}$ s$^{–1}$ hits the metal.

**Solution** According to Einstein's equation

Kinetic energy = ½ m$_e$ v$^2$=h(v – v$_0$ )

= (6.626 × 10$^{–34}$ J s) (1.0 × 10$^{15}$ s$^{–1}$ – 7.0 ×10$^{14}$ s$^{–1}$)

= (6.626 × 10$^{–34}$ J s) (10.0 × 10$^{14}$ s$^{–1}$ – 7.0 ×10$^{14}$ s$^{–1}$)

= (6.626 × 10$^{–34}$ J s) × (3.0 × 10$^{14}$ s$^{–1}$)

= 1.988 × 10$^{–19}$ J

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**2.3.3 Evidence for the quantized\* Electronic Energy Levels: Atomic spectra** The speed of light depends upon the nature of the medium through which it passes. As a result, the beam of light is deviated or refracted from its original path as it passes from one medium to another. It is observed that when a ray of white light is passed through a prism, the wave with shorter wavelength bends more than the one with a longer wavelength. Since ordinary white light consists of waves with all the wavelengths in the visible range, a ray of white light is spread out into a series of coloured bands called spectrum. The light of red colour which has longest wavelength is deviated the least while the violet light, which has shortest wavelength is deviated the most. The spectrum of white light, that we can see, ranges from violet at 7.50 × 10$^{14}$ Hz to red at 4×10$^{14}$ Hz. Such a spectrum is called continuous spectrum. Continuous because violet merges into blue, blue into green and so on. A similar spectrum is produced when a rainbow forms in the sky. Remember that visible light is just a small portion of the electromagnetic radiation (Fig.2.7). When electromagnetic radiation interacts with matter, atoms and molecules may absorb energy and reach to a higher energy state. With higher energy, these are in an unstable state. For returning to their normal (more stable, lower energy states) energy state, the atoms and molecules emit radiations in various regions of the electromagnetic spectrum.

**Emission and Absorption Spectra** The spectrum of radiation emitted by a substance that has absorbed energy is called an emission spectrum. Atoms, molecules or ions that have absorbed radiation are said to be "excited". To produce an emission spectrum, energy is supplied to a sample by heating it or irradiating it and the wavelength (or frequency) of the

radiation emitted, as the sample gives up the absorbed energy, is recorded. An absorption spectrum is like the photographic negative of an emission spectrum. A continuum of radiation is passed through a sample which absorbs radiation of certain wavelengths. The missing wavelength which corresponds to the radiation absorbed by the matter, leave dark spaces in the bright continuous spectrum. The study of emission or absorption spectra is referred to as spectroscopy. The spectrum of the visible light, as discussed above, was continuous as all wavelengths (red to violet) of the visible light are represented in the spectra. The emission spectra of atoms in the gas phase, on the other hand, do not show a continuous spread of wavelength from red to violet, rather they emit light only at specific wavelengths with dark spaces between them. Such spectra are called line spectra or atomic spectra because the emitted radiation is identified by the appearance of bright lines in the spectra (Fig. 2.10 page 45). Line emission spectra are of great interest in the study of electronic structure. Each element has a unique line emission spectrum. The characteristic lines in atomic spectra can be used in chemical analysis to identify unknown atoms in the same way as fingerprints are used to identify people. The exact matching of lines of the emission spectrum of the atoms of a known element with the lines from an unknown sample quickly establishes the identity of the latter, German chemist, Robert Bunsen (1811-1899) was one of the first investigators to use line spectra to identify elements. Elements like rubidium (Rb), caesium (Cs) thallium (Tl), indium (In), gallium (Ga) and scandium (Sc) were discovered when their minerals were analysed by spectroscopic methods. The element helium (He) was discovered in the sun by spectroscopic method. Line Spectrum of Hydrogen When an electric discharge is passed through gaseous hydrogen, the H2 molecules dissociate and the energetically excited hydrogen atoms produced emit electromagnetic radiation of discrete frequencies. The hydrogen spectrum consists of several series of lines named after their discoverers. Balmer showed in 1885 on the basis of experimental observations * The restriction of any property to discrete values is called quantization. Rationalised 2023-24 structure of atom 45 that if spectral lines are expressed in terms of wavenumber ( ), then the visible lines of the hydrogen spectrum obey the following formula: (2.8) where n is an integer equal to or greater than 3 (i.e., n = 3,4,5,....) The series of lines described by this formula are called the Balmer series. The Balmer series of lines are the only lines in the hydrogen spectrum which appear in the visible region of the electromagnetic spectrum. The Swedish spectroscopist, Johannes Rydberg, noted that all series of lines in the hydrogen spectrum could be described by the following expression : (2.9) where n1=1,2........ n2 = n1 + 1, n1 + 2...... The value 109,677 cm−1 is called the Rydberg constant for hydrogen. The first five series of lines that correspond to n1 = 1, 2, 3, 4, 5 are known as Lyman, Balmer, Paschen, Bracket and Pfund series, respectively, Table 2.3 shows these series of transitions in the hydrogen spectrum. Fig. 2.11 (page, 46) shows the Lyman, Balmer and Paschen series of transitions for hydrogen atom. Of all the elements, hydrogen atom has the simplest line spectrum. Line spectrum (a) (b) Fig. 2.10 (a) Atomic emission. The light emitted by a sample of excited hydrogen atoms (or any other element) can be passed through a prism and separated into certain discrete wavelengths. Thus an emission spectrum, which is a photographic recording of the separated wavelengths is called as line spectrum. Any sample of reasonable size contains an enormous number of atoms. Although a single atom can be in only one excited state at a time, the collection of atoms contains all possible excited states. The light emitted as these atoms fall to lower energy states is responsible for the spectrum. (b) Atomic absorption. When white light is passed through unexcited atomic hydrogen and then through a slit and prism, the transmitted light is lacking in intensity at the same wavelengths as are emitted in (a) The recorded absorption spectrum is also a line spectrum and the photographic negative of the emission spectrum. Table 2.3 The Spectral Lines for Atomic Hydrogen Series n1 n2 Spectral Region Lyman Balmer Paschen Brackett Pfund 1 2 3 4 5 2,3.... 3,4.... 4,5.... 5,6.... 6,7.... Ultraviolet Visible Infrared Infrared Infrared Rationalised 2023-24 46 chemistry becomes more and more complex for heavier atom. There are, however, certain features which are

common to all line spectra, i.e., (i) line spectrum of element is unique and (ii) there is regularity in the line spectrum of each element. The questions which arise are: What are the reasons for these similarities? Is it something to do with the electronic structure of atoms? These are the questions need to be answered. We shall find later that the answers to these questions provide the key in understanding electronic structure of these elements. 2.4 Bohr's Model for Hydrogen Atom Neils Bohr (1913) was the first to explain quantitatively the general features of the structure of hydrogen atom and its spectrum. He used Planck's concept of quantisation of energy. Though the theory is not the modern quantum mechanics, it can still be used to rationalize many points in the Fig. 2.11 Transitions of the electron in the hydrogen atom (The diagram shows the Lyman, Balmer and Paschen series of transitions) atomic structure and spectra. Bohr's model for hydrogen atom is based on the following postulates: i) The electron in the hydrogen atom can move around the nucleus in a circular path of fixed radius and energy. These paths are called orbits, stationary states or allowed energy states. These orbits are arranged concentrically around the nucleus. ii) The energy of an electron in the orbit does not change with time. However, the electron will move from a lower stationary state to a higher stationary state when required amount of energy is absorbed by the electron or energy is emitted when electron moves from higher stationary state to lower stationary state (equation 2.16). The energy change does not take place in a continuous manner. Angular Momentum Just as linear momentum is the product of mass (m) and linear velocity (v), angular momentum is the product of moment of inertia (I) and angular velocity (ω). For an electron of mass $m_e$ , moving in a circular path of radius r around the nucleus, angular momentum = I × ω Since I = $m_e$ $r^2$, and ω = v/r where v is the linear velocity, ∴angular momentum = $m_e$ $r^2$ × v/r = $m_e$ vr iii) The frequency of radiation absorbed or emitted when transition occurs between two stationary states that differ in energy by ΔE, is given by: (2.10) Where $E_1$ and $E_2$ are the energies of the lower and higher allowed energy states respectively. This expression is commonly known as Bohr's frequency rule. iv) The angular momentum of an electron is quantised. In a given stationary state it can be expressed as in equation (2.11) $m_e$ r n h e v  . 2- n = 1,2,3..... (2.11) Rationalised 2023-24 structure of atom 47 Where $m_e$ is the mass of electron, v is the velocity and r is the radius of the orbit in which electron is moving. Thus an electron can move only in those orbits for which its angular momentum is integral multiple of h/2π. That means angular momentum is quantised. Radiation is emitted or obsorbed only when transition of electron takes place from one quantised value of angular momentum to another. Therefore, Maxwell's electromagnetic theory does not apply here that is why only certain fixed orbits are allowed. The details regarding the derivation of energies of the stationary states used by Bohr, are quite complicated and will be discussed in higher classes. However, according to Bohr's theory for hydrogen atom: a) The stationary states for electron are numbered n = 1,2,3.......... These integral numbers (Section 2.6.2) are known as Principal quantum numbers. b) The radii of the stationary states are expressed as: $r_n$ = $n^2$ $a_0$ (2.12) where $a_0$ = 52.9 pm. Thus the radius of the first stationary state, called the Bohr orbit, is 52.9 pm. Normally the electron in the hydrogen atom is found in this orbit (that is n=1). As n increases the value of r will increase. In other words the electron will be present away from the nucleus. c) The most important property associated with the electron, is the energy of its stationary state. It is given by the expression. E n n H - 🔲 🔲 🔲 🔲 R 🔲 1 2 n = 1,2,3.... (2.13) where $R_H$ is called Rydberg constant and its value is $2.18 \times 10^{-18}$ J. The energy of the lowest state, also called as the ground state, is $E_1$ = $-2.18 \times 10^{-18}$ ( 1 $1^2$ ) = $-2.18 \times 10^{-18}$ J. The energy of the stationary state for n = 2, will be : $E_2$ = $-2.18 \times 10^{-18}$ J ( 1 $2^2$ )= $-0.545 \times 10^{-18}$ J. Fig. 2.11 depicts the energies of different stationary states or energy levels of hydrogen atom. This representation is called an energy level diagram. When the electron is free from the influence of nucleus, the energy is taken as zero. The electron in this situation is associated with the stationary state of Principal Quantum number = n = ∞ and is called as ionized hydrogen atom. When the electron is attracted by the nucleus and is present in orbit n, the energy is emitted and its

energy is lowered. That is the reason What does the negative electronic energy (En) for hydrogen atom mean? The energy of the electron in a hydrogen atom has a negative sign for all possible orbits (eq. 2.13). What does this negative sign convey? This negative sign means that the energy of the electron in the atom is lower than the energy of a free electron at rest. A free electron at rest is an electron that is infinitely far away from the nucleus and is assigned the energy value of zero. Mathematically, this corresponds to setting $n$ equal to infinity in the equation (2.13) so that $E_\infty = 0$. As the electron gets closer to the nucleus (as $n$ decreases), $E_n$ becomes larger in absolute value and more and more negative. The most negative energy value is given by $n=1$ which corresponds to the most stable orbit. We call this the ground state. Niels Bohr (1885–1962) Niels Bohr, a Danish physicist received his Ph.D. from the University of Copenhagen in 1911. He then spent a year with J.J. Thomson and Ernest Rutherford in England. In 1913, he returned to Copenhagen where he remained for the rest of his life. In 1920 he was named Director of the Institute of theoretical Physics. After first World War, Bohr worked energetically for peaceful uses of atomic energy. He received the first Atoms for Peace award in 1957. Bohr was awarded the Nobel Prize in Physics in 1922. Rationalised 2023-24

48 chemistry for the presence of negative sign in equation (2.13) and depicts its stability relative to the reference state of zero energy and $n = \infty$. d) Bohr's theory can also be applied to the ions containing only one electron, similar to that present in hydrogen atom. For example, He+ Li2+, Be3+ and so on. The energies of the stationary states associated with these kinds of ions (also known as hydrogen like species) are given by the expression.

$$E_n = -2.18 \times 10^{-18} \left( \frac{Z^2}{n^2} \right) J \quad (2.14)$$

and radii by the expression

$$r_n = \frac{52.9 \, (n^2)}{Z} \, pm \quad (2.15)$$

where Z is the atomic number and has values 2,3 for the helium and lithium atoms respectively. From the above equations, it is evident that the value of energy becomes more negative and that of radius becomes smaller with increase of Z. This means that electron will be tightly bound to the nucleus. e) It is also possible to calculate the velocities of electrons moving in these orbits. Although the precise equation is not given here, qualitatively the magnitude of velocity of electron increases with increase of positive charge on the nucleus and decreases with increase of principal quantum number. 2.4.1 Explanation of Line Spectrum of Hydrogen Line spectrum observed in case of hydrogen atom, as mentioned in section 2.3.3, can be explained quantitatively using Bohr's model. According to assumption 2, radiation (energy) is absorbed if the electron moves from the orbit of smaller Principal quantum number to the orbit of higher Principal quantum number, whereas the radiation (energy) is emitted if the electron moves from higher orbit to lower orbit. The energy gap between the two orbits is given by equation (2.16)

$$\Delta E = E_f - E_i \quad (2.16)$$

Combining equations (2.13) and (2.16)

$$E_{n_i} = -\frac{R_H}{n_i^2} \qquad E_{n_f} = -\frac{R_H}{n_f^2}$$

(where $n_i$ and $n_f$ stand for initial orbit and final orbits)

$$\Delta E = R_H \left( \frac{1}{n_i^2} \right) - \left( -R_H \frac{1}{n_f^2} \right) = 2.18 \times 10^{-18} J \left( \frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \quad (2.17)$$

The frequency ($\nu$) associated with the absorption and emission of the photon can be evaluated by using equation (2.18)

$$\nu = \frac{\Delta E}{h} = \frac{2.18 \times 10^{-18} J}{6.626 \times 10^{-34} Js} \left( \frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \quad (2.18)$$

$$= 3.29 \times 10^{15} \left( \frac{1}{n_i^2} - \frac{1}{n_f^2} \right) Hz \quad (2.19)$$

and in terms of wavenumbers ($\bar{\nu}$)

$$\bar{\nu} = \frac{\nu}{c} = \frac{3.29 \times 10^{15} \, s^{-1}}{3 \times 10^8 \, m \, s^{-1}} \left( \frac{1}{n_i^2} - \frac{1}{n_f^2} \right) \quad (2.20)$$

$$= 1.09677 \times 10^7 \left( \frac{1}{n_i^2} - \frac{1}{n_f^2} \right) m^{-1} \quad (2.21)$$

In case of absorption spectrum, $n_f > n_i$ and the term in the parenthesis is positive and energy is absorbed. On the other hand in case of emission spectrum $n_i > n_f$, $\Delta E$ is negative and energy is released. The expression (2.17) is similar to that used by Rydberg (2.9) derived empirically using the experimental data available at that time. Further, each spectral line, whether in absorption or emission spectrum, can be associated to the particular transition in hydrogen atom. In case of large number of hydrogen atoms, different possible transitions can be observed and thus leading to large number of spectral lines. The brightness or intensity of spectral lines depends upon the number of photons of same wavelength or frequency absorbed or emitted. Rationalised 2023-24 structure of atom 49 Problem 2.10 What are the frequency and wavelength of a photon emitted during a transition from n = 5 state to the n = 2 state in the hydrogen atom? Solution Since $n_i = 5$ and $n_f = 2$, this transition gives rise to a spectral line in

the visible region of the Balmer series. From equation (2.17) E = = 2 18 10 1 5 1 2 4 58 10 18 2 2 19 . . - ⬜ ⬜ ⬜ ⬜ ⬜ ⬜ ⬜ - ⬜ ⬜ J J It is an emission energy The frequency of the photon (taking energy in terms of magnitude) is given by = 6.91×1014 Hz Problem 2.11 Calculate the energy associated with the first orbit of He+. What is the radius of this orbit? Solution E Z n n J - ⬜ - ( . 2 18 10 ) 18 2 2 atom–1 For He+, n = 1, Z = 2 E1 18 2 2 2 18 10 2 18 1 - 8 72 10 ⬜ - ⬜ - - ( . )( ) . J J The radius of the orbit is given by equation (2.15) r nm n n Z = ( . 0 0529 ) 2 Since n = 1, and Z = 2 r nm n = = nm ( . ) . 0 0529 1 2 0 02645 2 2.4.2 Limitations of Bohr's Model Bohr's model of the hydrogen atom was no doubt an improvement over Rutherford's nuclear model, as it could account for the stability and line spectra of hydrogen atom and hydrogen like ions (for example, He+, Li2+, Be3+, and so on). However, Bohr's model was too simple to account for the following points. i) It fails to account for the finer details (doublet, that is two closely spaced lines) of the hydrogen atom spectrum observed by using sophisticated spectroscopic techniques. This model is also unable to explain the spectrum of atoms other than hydrogen, for example, helium atom which possesses only two electrons. Further, Bohr's theory was also unable to explain the splitting of spectral lines in the presence of magnetic field (Zeeman effect) or an electric field (Stark effect). ii) It could not explain the ability of atoms to form molecules by chemical bonds. In other words, taking into account the points mentioned above, one needs a better theory which can explain the salient features of the structure of complex atoms. 2.5 Towards Quantum Mechanical Model of the Atom In view of the shortcoming of the Bohr's model, attempts were made to develop a more suitable and general model for atoms. Two important developments which contributed significantly in the formulation of such a model were: 1. Dual behaviour of matter, 2. Heisenberg uncertainty principle. 2.5.1 Dual Behaviour of Matter The French physicist, de Broglie, in 1924 proposed that matter, like radiation, should also exhibit dual behaviour i.e., both particle and wavelike properties. This means that just as the photon has momentum as well as wavelength, electrons should also have momentum as well as wavelength, de Broglie, from this analogy, gave the following relation between wavelength (λ) and momentum (p) of a material particle. Rationalised 2023-24 50 chemistry Solution According to de Brogile equation (2.22) - - ⬜ ⬜ ⬜ h mv Js kg m s ( . ) ( . )( ) 6 626 10 0 1 10 34 1 = 6.626 × 10–34 m (J = kg m2 s–2) Problem 2.13 The mass of an electron is 9.1×10–31 kg. If its K.E. is 3.0×10–25 J, calculate its wavelength. Solution Since K.E. = ½ mv2 v K E kg m s kg = = 2 2 3 0 10 9 1 10 1 2 25 2 2 31 1 2 . . . . / / m - ⬜ ⬜ ⬜ ⬜ ⬜ ⬜ ⬜ - ⬜ ⬜ ⬜ ⬜ ⬜ ⬜ = 812 m s–1 h m v 6.626 10 Js 34 ( . 9 1 10 812 kg )( m s ) 31 1 = 8967 × 10–10 m = 896.7 nm Problem 2.14 Calculate the mass of a photon with wavelength 3.6 Å. Solution λ = 3.6 Å = 3.6 × 10–10 m Velocity of photon = velocity of light 34 10 8 1 = 6.135 × 10–29 kg - - h m h v p (2.22) where m is the mass of the particle, v its velocity and p its momentum. de Broglie's prediction was confirmed experimentally when it was found that an electron beam undergoes diffraction, a phenomenon characteristic of waves. This fact has been put to use in making an electron microscope, which is based on the wavelike behaviour of electrons just as an ordinary microscope utilises the wave nature of light. An electron microscope is a powerful tool in modern scientific research because it achieves a magnification of about 15 million times. It needs to be noted that according to de Broglie, every object in motion has a wave character. The wavelengths associated with ordinary objects are so short (because of their large masses) that their wave properties cannot be detected. The wavelengths associated with electrons and other subatomic particles (with very small mass) can however be detected experimentally. Results obtained from the following problems prove these points qualitatively. Problem 2.12 What will be the wavelength of a ball of mass 0.1 kg moving with a velocity of 10 m s–1 ? 2.5.2 Heisenberg's Uncertainty Principle Werner Heisenberg a German physicist in 1927, stated uncertainty principle which is the consequence of dual behaviour of matter and radiation. It states that it is impossible to determine simultaneously, the exact position and exact momentum (or velocity) of an electron. Mathematically, it can be given as in equation (2.23). Louis de Broglie (1892–1987) Louis de Broglie, a French physicist, studied history as an undergraduate in

the early 1910's. His interest turned to science as a result of his assignment to radio communications in World War I. He received his Dr. Sc. from the University of Paris in 1924. He was professor of theoretical physics at the University of Paris from 1932 untill his retirement in 1962. He was awarded the Nobel Prize in Physics in 1929. Rationalised 2023-24 structure of atom 51 (2.23) where $\Delta x$ is the uncertainty in position and $\Delta p_x$ (or $\Delta v_x$) is the uncertainty in momentum (or velocity) of the particle. If the position of the electron is known with high degree of accuracy ($\Delta x$ is small), then the velocity of the electron will be uncertain [$\Delta(v_x)$ is large]. On the other hand, if the velocity of the electron is known precisely ($\Delta(v_x)$ is small), then the position of the electron will be uncertain ($\Delta x$ will be large). Thus, if we carry out some physical measurements on the electron's position or velocity, the outcome will always depict a fuzzy or blur picture. The uncertainty principle can be best understood with the help of an example. Suppose you are asked to measure the thickness of a sheet of paper with an unmarked metrestick. Obviously, the results obtained would be extremely inaccurate and meaningless. In order to obtain any accuracy, you should use an instrument graduated in units smaller than the thickness of a sheet of the paper. Analogously, in order to determine the position of an electron, we must use a meterstick calibrated in units of smaller than the dimensions of electron (keep in mind that an electron is considered as a point charge and is therefore, dimensionless). To observe an electron, we can illuminate it with "light" or electromagnetic radiation. The "light" used must have a wavelength smaller than the dimensions of an electron. The high momentum photons of such light $p h= - \square \square \square \square \square$ would change the energy of electrons by collisions. In this process we, no doubt, would be able to calculate the position of the electron, but we would know very little about the velocity of the electron after the collision. Significance of Uncertainty Principle One of the important implications of the Heisenberg Uncertainty Principle is that it rules out existence of definite paths or trajectories of electrons and other similar particles. The trajectory of an object is determined by its location and velocity at various moments. If we know where a body is at a particular instant and if we also know its velocity and the forces acting on it at that instant, we can tell where the body would be sometime later. We, therefore, conclude that the position of an object and its velocity fix its trajectory. Since for a sub-atomic object such as an electron, it is not possible simultaneously to determine the position and velocity at any given instant to an arbitrary degree of precision, it is not possible to talk of the trajectory of an electron. The effect of Heisenberg Uncertainty Principle is significant only for motion of microscopic objects and is negligible for that of macroscopic objects. This can be seen from the following examples. If uncertainty principle is applied to an object of mass, say about a milligram (10–6 kg), then Werner Heisenberg (1901–1976) Werner Heisenberg (1901–1976) received his Ph.D. in physics from the University of Munich in 1923. He then spent a year working with Max Born at Gottingen and three years with Niels Bohr in Copenhagen. He was professor of physics at the University of Leipzig from 1927 to 1941. During World War II, Heisenberg was in charge of German research on the atomic bomb. After the war he was named director of Max Planck Institute for physics in Gottingen. He was also accomplished mountain climber. Heisenberg was awarded the Nobel Prize in Physics in 1932. Rationalised 2023-24 52 chemistry The value of $\Delta v \Delta x$ obtained is extremely small and is insignificant. Therefore, one may say that in dealing with milligramsized or heavier objects, the associated uncertainties are hardly of any real consequence. In the case of a microscopic object like an electron on the other hand. $\Delta v.\Delta x$ obtained is much larger and such uncertainties are of real consequence. For example, for an electron whose mass is 9.11×10–31 kg., according to Heisenberg uncertainty principle It, therefore, means that if one tries to find the exact location of the electron, say to an uncertainty of only 10–8 m, then the uncertainty $\Delta v$ in velocity would be 10 10 10 4 2 1 8 4 1 $-$ m s m ms which is so large that the classical picture of electrons moving in Bohr's orbits (fixed) cannot hold good. It, therefore, means that the precise statements of the position and momentum of electrons have to be replaced by the statements of probability, that the electron has at a given position and momentum. This is what

happens in the quantum mechanical model of atom. = $0.579 \times 10^7$ m s$^{-1}$ (1J = 1 kg m$^2$ s$^{-2}$) = $5.79 \times 10^6$ m s$^{-1}$ Problem 2.16 A golf ball has a mass of 40g, and a speed of 45 m/s. If the speed can be measured within accuracy of 2%, calculate the uncertainty in the position. Solution The uncertainty in the speed is 2%, i.e., Using the equation (2.22) = $1.46 \times 10^{-33}$ m This is nearly ~ $10^{18}$ times smaller than the diameter of a typical atomic nucleus. As mentioned earlier for large particles, the uncertainty principle sets no meaningful limit to the precision of measurements. Reasons for the Failure of the Bohr Model One can now understand the reasons for the failure of the Bohr model. In Bohr model, an electron is regarded as a charged particle moving in well defined circular orbits about the nucleus. The wave character of the electron is not considered in Bohr model. Further, an orbit is a clearly defined path and this path can completely be defined only if both the position and the velocity of the electron are known exactly at the same time. This is not possible according to the Heisenberg uncertainty principle. Bohr model of the hydrogen atom, therefore, not only ignores dual behaviour of matter but also contradicts Heisenberg uncertainty principle. Problem 2.15 A microscope using suitable photons is employed to locate an electron in an atom within a distance of 0.1 Å. What is the uncertainty involved in the measurement of its velocity? Solution $\Delta x \Delta p$ = or $\Delta x$ m$\Delta$ v Rationalised 2023-24 structure of atom 53 In view of these inherent weaknesses in the Bohr model, there was no point in extending Bohr model to other atoms. In fact an insight into the structure of the atom was needed which could account for wave-particle duality of matter and be consistent with Heisenberg uncertainty principle. This came with the advent of quantum mechanics.

2.6 Quantum Mechanical Model of Atom Classical mechanics, based on Newton's laws of motion, successfully describes the motion of all macroscopic objects such as a falling stone, orbiting planets etc., which have essentially a particle-like behaviour as shown in the previous section. However it fails when applied to microscopic objects like electrons, atoms, molecules etc. This is mainly because of the fact that classical mechanics ignores the concept of dual behaviour of matter especially for sub-atomic particles and the uncertainty principle. The branch of science that takes into account this dual behaviour of matter is called quantum mechanics. Quantum mechanics is a theoretical science that deals with the study of the motions of the microscopic objects that have both observable wave like and particle like properties. It specifies the laws of motion that these objects obey. When quantum mechanics is applied to macroscopic objects (for which wave like properties are insignificant) the results are the same as those from the classical mechanics. Quantum mechanics was developed independently in 1926 by Werner Heisenberg and Erwin Schrödinger. Here, however, we shall be discussing the quantum mechanics which is based on the ideas of wave motion. The fundamental equation of quantum mechanics was developed by Schrödinger and it won him the Nobel Prize in Physics in 1933. This equation which incorporates waveparticle duality of matter as proposed by de Broglie is quite complex and knowledge of higher mathematics is needed to solve it. You will learn its solutions for different systems in higher classes. For a system (such as an atom or a molecule whose energy does not change with time) the Schrödinger equation is written as where is a mathematical operator called Hamiltonian. Schrödinger gave a recipe of constructing this operator from the expression for the total energy of the system. The total energy of the system takes into account the kinetic energies of all the sub-atomic particles (electrons, nuclei), attractive potential between the electrons and nuclei and repulsive potential among the electrons and nuclei individually. Solution of this equation gives E and $\psi$. Hydrogen Atom and the Schrödinger Equation When Schrödinger equation is solved for hydrogen atom, the solution gives the possible energy levels the electron can occupy and the corresponding wave function(s) ($\psi$) of the electron associated with each energy level. These quantized energy states and corresponding wave functions which are characterized by a set of three quantum numbers (principal quantum number n, azimuthal quantum number l and magnetic quantum number ml ) arise as a natural consequence in the solution of the Schrödinger equation. When an electron is in any energy state, the wave function Erwin Schrödinger,

an Austrian physicist received his Ph.D. in theoretical physics from the University of Vienna in 1910. In 1927 Schrödinger succeeded Max Planck at the University of Berlin at Planck's request. In 1933, Schrödinger left Berlin because of his opposition to Hitler and Nazi policies and returned to Austria in 1936. After the invasion of Austria by Germany, Schrödinger was forcibly removed from his professorship. He then moved to Dublin, Ireland where he remained for seventeen years. Schrödinger shared the Nobel Prize for Physics with P.A.M. Dirac in 1933. Erwin Schrödinger (1887–1961) Rationalised 2023-24 54 chemistry corresponding to that energy state contains all information about the electron. The wave function is a mathematical function whose value depends upon the coordinates of the electron in the atom and does not carry any physical meaning. Such wave functions of hydrogen or hydrogen like species with one electron are called atomic orbitals. Such wave functions pertaining to one-electron species are called one-electron systems. The probability of finding an electron at a point within an atom is proportional to the $|\psi|^2$ at that point. The quantum mechanical results of the hydrogen atom successfully predict all aspects of the hydrogen atom spectrum including some phenomena that could not be explained by the Bohr model. Application of Schrödinger equation to multi-electron atoms presents a difficulty: the Schrödinger equation cannot be solved exactly for a multi-electron atom. This difficulty can be overcome by using approximate methods. Such calculations with the aid of modern computers show that orbitals in atoms other than hydrogen do not differ in any radical way from the hydrogen orbitals discussed above. The principal difference lies in the consequence of increased nuclear charge. Because of this all the orbitals are somewhat contracted. Further, as you shall see later (in subsections 2.6.3 and 2.6.4), unlike orbitals of hydrogen or hydrogen like species, whose energies depend only on the quantum number n, the energies of the orbitals in multi-electron atoms depend on quantum numbers n and l. Important Features of the Quantum Mechanical Model of Atom Quantum mechanical model of atom is the picture of the structure of the atom, which emerges from the application of the Schrödinger equation to atoms. The following are the important features of the quantum-mechanical model of atom: 1. The energy of electrons in atoms is quantized (i.e., can only have certain specific values), for example when electrons are bound to the nucleus in atoms. 2. The existence of quantised electronic energy levels is a direct result of the wave like properties of electrons and are allowed solutions of Schrödinger wave equation. 3. Both the exact position and exact velocity of an electron in an atom cannot be determined simultaneously (Heisenberg uncertainty principle). The path of an electron in an atom therefore, can never be determined or known accurately. That is why, as you shall see later on, one talks of only probability of finding the electron at different points in an atom. 4. An atomic orbital is the wave function $\psi$ for an electron in an atom. Whenever an electron is described by a wave function, we say that the electron occupies that orbital. Since many such wave functions are possible for an electron, there are many atomic orbitals in an atom. These "one electron orbital wave functions" or orbitals form the basis of the electronic structure of atoms. In each orbital, the electron has a definite energy. An orbital cannot contain more than two electrons. In a multi-electron atom, the electrons are filled in various orbitals in the order of increasing energy. For each electron of a multi-electron atom, there shall, therefore, be an orbital wave function characteristic of the orbital it occupies. All the information about the electron in an atom is stored in its orbital wave function $\psi$ and quantum mechanics makes it possible to extract this information out of $\psi$. 5. The probability of finding an electron at a point within an atom is proportional to the square of the orbital wave function i.e., $|\psi|^2$ at that point. $|\psi|^2$ is known as probability density and is always positive. From the value of $|\psi|^2$ at different points within an atom, it is possible to predict the region around the nucleus where electron will most probably be found. 2.6.1 Orbitals and Quantum Numbers A large number of orbitals are possible in an atom. Qualitatively these orbitals can Rationalised 2023-24 structure of atom 55 be distinguished by their size, shape and orientation. An orbital of smaller size means there is more chance of finding the electron near the nucleus. Similarly shape and orientation

mean that there is more probability of finding the electron along certain directions than along others. Atomic orbitals are precisely distinguished by what are known as quantum numbers. Each orbital is designated by three quantum numbers labelled as n, l and ml . The principal quantum number 'n' is a positive integer with value of n = 1,2,3....... The principal quantum number determines the size and to large extent the energy of the orbital. For hydrogen atom and hydrogen like species (He+, Li2+, .... etc.) energy and size of the orbital depends only on 'n'. The principal quantum number also identifies the shell. With the increase in the value of 'n', the number of allowed orbital increases and are given by 'n2' All the orbitals of a given value of 'n' constitute a single shell of atom and are represented by the following letters n = 1 2 3 4 ............ Shell = K L M N ............ Size of an orbital increases with increase of principal quantum number 'n'. In other words the electron will be located away from the nucleus. Since energy is required in shifting away the negatively charged electron from the positively charged nucleus, the energy of the orbital will increase with increase of n. Azimuthal quantum number. 'l' is also known as orbital angular momentum or subsidiary quantum number. It defines the three-dimensional shape of the orbital. For a given value of n, l can have n values ranging from 0 to n − 1, that is, for a given value of n, the possible value of l are : l = 0, 1, 2, .......... (n–1) For example, when n = 1, value of l is only 0. For n = 2, the possible value of l can be 0 and 1. For n = 3, the possible l values are 0, 1 and 2. Each shell consists of one or more sub-shells or sub-levels. The number of sub-shells in a principal shell is equal to the value of n. For example in the first shell (n = 1), there is only one sub-shell which corresponds to l = 0. There are two sub-shells (l = 0, 1) in the second shell (n = 2), three (l = 0, 1, 2) in third shell (n = 3) and so on. Each sub-shell is assigned an azimuthal quantum number (l). Sub-shells corresponding to different values of l are represented by the following symbols. Value for l : 0 1 2 3 4 5 ............ notation for s p d f g h ............ sub-shell Table 2.4 shows the permissible values of 'l ' for a given principal quantum number and the corresponding sub-shell notation. Magnetic orbital quantum number. 'ml ' gives information about the spatial orientation of the orbital with respect to standard set of co-ordinate axis. For any sub-shell (defined by 'l' value) 2l+1 values of ml are possible and these values are given by : ml = − l, − (l −1), − (l–2)... 0,1... (l –2), (l–1), l Thus for l = 0, the only permitted value of ml = 0, [2(0)+1 = 1, one s orbital]. For l = 1, ml can be −1, 0 and +1 [2(1)+1 = 3, three p orbitals]. For l = 2, ml = −2, −1, 0, +1 and +2, [2(2)+1 = 5, five d orbitals]. It should be noted that the values of ml are derived from l and that the value of l are derived from n. Table 2.4 Subshell Notations n l Subshell notation 1 2 2 3 3 3 4 4 4 4 0 0 1 0 1 2 0 1 2 3 1s 2s 2p 3s 3p 3d 4s 4p 4d 4f Rationalised 2023-24 56 chemistry Each orbital in an atom, therefore, is defined by a set of values for n, l and ml . An orbital described by the quantum numbers n = 2, l = 1, ml = 0 is an orbital in the p subshell of the second shell. The following chart gives the relation between the subshell and the number of orbitals associated with it. Value of l 0 1 2 3 4 5 Subshell notation s p d f g h number of orbitals 1 3 5 7 9 11 Electron spin 's' : The three quantum numbers labelling an atomic orbital can be used equally well to define its energy, shape and orientation. But all these quantum numbers are not enough to explain the line spectra observed in the case of multi-electron atoms, that is, some of the lines actually occur in doublets (two lines closely spaced), triplets (three lines, closely spaced) etc. This suggests the presence of a few more energy levels than predicted by the three quantum numbers. In 1925, George Uhlenbeck and Samuel Goudsmit proposed the presence of the fourth quantum number known as the electron spin quantum number (ms). An electron spins around its own axis, much in a similar way as earth spins around its own axis while revolving around the sun. In other words, an electron has, besides charge and mass, intrinsic spin angular quantum number. Spin angular momentum of the electron — a vector quantity, can have two orientations relative to the chosen axis. These two orientations are distinguished by the spin quantum numbers ms which can take the values of +½ or −½. These are called the two spin states of the electron and are normally represented by two arrows, ↑ (spin up) and ↓ (spin down). Two electrons that have different ms

values (one +½ and the other −½) are said to have opposite spins. An orbital cannot hold more than two electrons and these two electrons should have opposite spins. To sum up, the four quantum numbers provide the following information : i) n defines the shell, determines the size of the orbital and also to a large extent the energy of the orbital. ii) There are n subshells in the nth shell. l identifies the subshell and determines the shape of the orbital (see section 2.6.2). There are (2l+1) orbitals of each type in a subshell, that is, one s orbital (l = 0), three p orbitals (l = 1) and five d orbitals (l = 2) per subshell. To some extent l also determines the energy of the orbital in a multi-electron atom. iii) ml designates the orientation of the orbital. For a given value of l, ml has (2l+1) values, the same as the number of orbitals per subshell. It means that Orbit, orbital and its importance Orbit and orbital are not synonymous. An orbit, as proposed by Bohr, is a circular path around the nucleus in which an electron moves. A precise description of this path of the electron is impossible according to Heisenberg uncertainty principle. Bohr orbits, therefore, have no real meaning and their existence can never be demonstrated experimentally. An atomic orbital, on the other hand, is a quantum mechanical concept and refers to the one electron wave function $\psi$ in an atom. It is characterized by three quantum numbers (n, l and ml ) and its value depends upon the coordinates of the electron. $\psi$ has, by itself, no physical meaning. It is the square of the wave function i.e., $|\psi|^2$ which has a physical meaning. $|\psi|^2$ at any point in an atom gives the value of probability density at that point. Probability density ($|\psi|^2$) is the probability per unit volume and the product of $|\psi|^2$ and a small volume (called a volume element) yields the probability of finding the electron in that volume (the reason for specifying a small volume element is that $|\psi|^2$ varies from one region to another in space but its value can be assumed to be constant within a small volume element). The total probability of finding the electron in a given volume can then be calculated by the sum of all the products of $|\psi|^2$ and the corresponding volume elements. It is thus possible to get the probable distribution of an electron in an orbital. Rationalised 2023-24 structure of atom 57 the number of orbitals is equal to the number of ways in which they are oriented. iv) ms refers to orientation of the spin of the electron. According to the German physicist, Max Born, the square of the wave function (i.e.,$\psi^2$ ) at a point gives the probability density of the electron at that point. The variation of $\psi^2$ as a function of r for 1s and 2s orbitals is given in Fig. 2.12(b). Here again, you may note that the curves for 1s and 2s orbitals are different. It may be noted that for 1s orbital the probability density is maximum at the nucleus and it decreases sharply as we move away from it. On the other hand, for 2s orbital the probability density first decreases sharply to zero and again starts increasing. After reaching a small maxima it decreases again and approaches zero as the value of r increases further. The region where this probability density function reduces to zero is called nodal surfaces or simply nodes. In general, it has been found that ns-orbital has (n − 1) nodes, that is, number of nodes increases with increase of principal quantum number n. In other words, number of nodes for 2s orbital is one, two for 3s and so on. These probability density variation can be visualised in terms of charge cloud diagrams [Fig. 2.13(a)]. In these diagrams, the density Fig. 2.12 The plots of (a) the orbital wave function $\psi(r)$; (b) the variation of probability density $\psi^2(r)$ as a function of distance r of the electron from the nucleus for 1s and 2s orbitals. Problem 2.17 What is the total number of orbitals associated with the principal quantum number n = 3 ? Solution For n = 3, the possible values of l are 0, 1 and 2. Thus there is one 3s orbital (n = 3, l = 0 and ml = 0); there are three 3p orbitals (n = 3, l = 1 and ml = −1, 0, +1); there are five 3d orbitals (n = 3, l = 2 and ml = −2, −1, 0, +1+, +2). Therefore, the total number of orbitals is 1+3+5 = 9 The same value can also be obtained by using the relation; number of orbitals = $n^2$, i.e. $3^2$ = 9. Problem 2.18 Using s, p, d, f notations, describe the orbital with the following quantum numbers (a) n = 2, l = 1, (b) n = 4, l = 0, (c) n = 5, l = 3, (d) n = 3, l = 2 Solution n l orbital a) 2 1 2p b) 4 0 4s c) 5 3 5f d) 3 2 3d 2.6.2 Shapes of Atomic Orbitals The orbital wave function or $\psi$ for an electron in an atom has no physical meaning. It is simply a mathematical function of the coordinates of the electron. However, for different orbitals the plots of

corresponding wave functions as a function of r (the distance from the nucleus) are different. Fig. 2.12(a), gives such plots for 1s (n = 1, l = 0) and 2s (n = 2, l = 0) orbitals. Rationalised 2023-24 58 chemistry of the dots in a region represents electron probability density in that region. Boundary surface diagrams of constant probability density for different orbitals give a fairly good representation of the shapes of the orbitals. In this representation, a boundary surface or contour surface is drawn in space for an orbital on which the value of probability density $|\psi|^2$ is constant. In principle many such boundary surfaces may be possible. However, for a given orbital, only that boundary surface diagram of constant probability density* is taken to be good representation of the shape of the orbital which encloses a region or volume in which the probability of finding the electron is very high, say, 90%. The boundary surface diagram for 1s and 2s orbitals are given in Fig. 2.13(b). One may ask a question : Why do we not draw a boundary surface diagram, which bounds a region in which the probability of finding the electron is, 100 %? The answer to this question is that the probability density $|\psi|^2$ has always some value, howsoever small it may be, at any finite distance from the nucleus. It is therefore, not possible to draw a boundary surface diagram of a rigid size in which the probability of finding the electron is 100%. Boundary surface diagram for a s orbital is actually a sphere centred on the nucleus. In two dimensions, this sphere looks like a circle. It encloses a region in which probability of finding the electron is about 90%. Thus, we see that 1s and 2s orbitals are spherical in shape. In reality all the s-orbitals are spherically symmetric, that is, the probability of finding the electron at a given distance is equal in all the directions. It is also observed that the size of the s orbital increases with increase in n, that is, 4s > 3s > 2s > 1s and the electron is located further away from the nucleus as the principal quantum number increases. Boundary surface diagrams for three 2p orbitals (l = 1) are shown in Fig. 2.14. In these diagrams, the nucleus is at the origin. Here, unlike s-orbitals, the boundary surface diagrams are not spherical. Instead each p orbital consists of two sections called lobes that are on either side of the plane that passes through the nucleus. The probability density * If probability density $|\psi|^2$ is constant on a given surface, $|\psi|$ is also constant over the surface. The boundary surface for $|\psi|^2$ and $|\psi|$ are identical. Fig. 2.14 Boundary surface diagrams of the three 2p orbitals. Fig. 2.13 (a) Probability density plots of 1s and 2s atomic orbitals. The density of the dots represents the probability density of finding the electron in that region. (b) Boundary surface diagram for 1s and 2s orbitals. Rationalised 2023-24 structure of atom 59 function is zero on the plane where the two lobes touch each other. The size, shape and energy of the three orbitals are identical. They differ however, in the way the lobes are oriented. Since the lobes may be considered to lie along the x, y or z axis, they are given the designations 2p$_x$, 2p$_y$, and 2p$_z$. It should be understood, however, that there is no simple relation between the values of m$_l$ (−1, 0 and +1) and the x, y and z directions. For our purpose, it is sufficient to remember that, because there are three possible values of m$_l$, there are, therefore, three p orbitals whose axes are mutually perpendicular. Like s orbitals, p orbitals increase in size and energy with increase in the principal quantum number and hence the order of the energy and size of various p orbitals is 4p > 3p > 2p. Further, like s orbitals, the probability density functions for p-orbital also pass through value zero, besides at zero and infinite distance, as the distance from the nucleus increases. The number of nodes are given by the n −2, that is number of radial node is 1 for 3p orbital, two for 4p orbital and so on. For l = 2, the orbital is known as d-orbital and the minimum value of principal quantum number (n) has to be 3. as the value of l cannot be greater than n−1. There are five m$_l$ values (−2, −1, 0, +1 and +2) for l = 2 and thus there are five d orbitals. The boundary surface diagram of d orbitals are shown in Fig. 2.15. The five d-orbitals are designated as d$_{xy}$, d$_{yz}$, d$_{xz}$, d$_{x^2–y^2}$ and d$_{z^2}$. The shapes of the first four d-orbitals are similar to each other, where as that of the fifth one, d$_{z^2}$, is different from others, but all five 3d orbitals are equivalent in energy. The d orbitals for which n is greater than 3 (4d, 5d...) also have shapes similar to 3d orbital, but differ in energy and size. Besides the radial nodes (i.e., probability density function is zero), the probability density functions for the np and nd

orbitals are zero at the plane (s), passing through the nucleus (origin). For example, in case of pz orbital, xy-plane is a nodal plane, in case of dxy orbital, there are two nodal planes passing through the origin and bisecting the xy plane containing z-axis. These are called angular nodes and number of angular nodes are given by 'l', i.e., one angular node for p orbitals, two angular nodes for 'd' orbitals and so on. The total number of nodes are given by (n–1), i.e., sum of l angular nodes and (n – l – 1) radial nodes. 2.6.3 Energies of Orbitals The energy of an electron in a hydrogen atom is determined solely by the principal quantum Fig. 2.15 Boundary surface diagrams of the five 3d orbitals. Rationalised 2023-24 60 chemistry number. Thus the energy of the orbitals in hydrogen atom increases as follows : 1s < 2s = 2p < 3s = 3p = 3d < (2.23) and is depicted in Fig. 2.16. Although the shapes of 2s and 2p orbitals are different, an electron has the same energy when it is in the 2s orbital as when it is present in 2p orbital. The orbitals having the same energy are called degenerate. The 1s orbital in a hydrogen atom, as said earlier, corresponds to the most stable condition and is called the ground state and an electron residing in this orbital is most strongly held by the nucleus. An electron in the 2s, 2p or higher orbitals in a hydrogen atom is in excited state. The energy of an electron in a multielectron atom, unlike that of the hydrogen atom, depends not only on its principal quantum number (shell), but also on its azimuthal quantum number (subshell). That is, for a given principal quantum number, s, p, d, f ... all have different energies. Within a given principal quantum number, the energy of orbitals increases in the order s<p<d E2s (Li) > E2s (Na) > E2s (K). 2.6.4 Filling of Orbitals in Atom The filling of electrons into the orbitals of different atoms takes place according to the aufbau principle which is based on the Pauli's exclusion principle, the Hund's rule of maximum multiplicity and the relative energies of the orbitals. Aufbau Principle The word 'aufbau' in German means 'building up'. The building up of orbitals means the Table 2.5 Arrangement of Orbitals with Increasing Energy on the Basis of (n+l) Rule Rationalised 2023-24 62 chemistry filling up of orbitals with electrons. The principle states : In the ground state of the atoms, the orbitals are filled in order of their increasing energies. In other words, electrons first occupy the lowest energy orbital available to them and enter into higher energy orbitals only after the lower energy orbitals are filled. As you have learnt above, energy of a given orbital depends upon effective nuclear charge and different type of orbitals are affected to different extent. Thus, there is no single ordering of energies of orbitals which will be universally correct for all atoms. However, following order of energies of the orbitals is extremely useful: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 4f, 5d, 6p, 7s... The order may be remembered by using the method given in Fig. 2.17. Starting from the top, the direction of the arrows gives the order of filling of orbitals, that is starting from right top to bottom left. With respect to placement of outermost valence electrons, it is remarkably accurate for all atoms. for example, valence electron in potassium must choose between 3d and 4s orbitals and as predicted by this sequence, it is found in 4s orbital. The above order should be assumed to be a rough guide to the filling of energy levels. In many cases, the orbitals are similar in energy and small changes in atomic structure may bring about a change in the order of filling. Even then, the above series is a useful guide to the building of the electronic structure of an atom provided that it is remembered that exceptions may occur. Pauli Exclusion Principle The number of electrons to be filled in various orbitals is restricted by the exclusion principle, given by the Austrian scientist Wolfgang Pauli (1926). According to this principle : No two electrons in an atom can have the same set of four quantum numbers. Pauli exclusion principle can also be stated as : "Only two electrons may exist in the same orbital and these electrons must have opposite spin." This means that the two electrons can have the same value of three quantum numbers n, l and ml , but must have the opposite spin quantum number. The restriction imposed by Pauli's exclusion principle on the number of electrons in an orbital helps in calculating the capacity of electrons to be present in any subshell. For example, subshell 1s comprises one orbital and thus the maximum number of electrons present in 1s subshell can be two, in p and d subshells, the maximum number of electrons can be 6 and 10 and so on. This

can be summed up as : the maximum number of electrons in the shell with principal quantum number n is equal to $2n^2$. Hund's Rule of Maximum Multiplicity This rule deals with the filling of electrons into the orbitals belonging to the same subshell (that is, orbitals of equal energy, called degenerate orbitals). It states : pairing of Fig.2.17 Order of filling of orbitals Rationalised 2023-24 structure of atom 63 electrons in the orbitals belonging to the same subshell (p, d or f) does not take place until each orbital belonging to that subshell has got one electron each i.e., it is singly occupied. Since there are three p, five d and seven f orbitals, therefore, the pairing of electrons will start in the p, d and f orbitals with the entry of 4th, 6th and 8th electron, respectively. It has been observed that half filled and fully filled degenerate set of orbitals acquire extra stability due to their symmetry (see Section, 2.6.7). 2.6.5 Electronic Configuration of Atoms The distribution of electrons into orbitals of an atom is called its electronic configuration. If one keeps in mind the basic rules which govern the filling of different atomic orbitals, the electronic configurations of different atoms can be written very easily. The electronic configuration of different atoms can be represented in two ways. For example : (i) $sa$ $pbdc$ ...... notation (ii) Orbital diagram s p d In the first notation, the subshell is represented by the respective letter symbol and the number of electrons present in the subshell is depicted, as the super script, like a, b, c, ... etc. The similar subshell represented for different shells is differentiated by writing the principal quantum number before the respective subshell. In the second notation each orbital of the subshell is represented by a box and the electron is represented by an arrow ($\uparrow$) a positive spin or an arrow ($\downarrow$) a negative spin. The advantage of second notation over the first is that it represents all the four quantum numbers. The hydrogen atom has only one electron which goes in the orbital with the lowest energy, namely 1s. The electronic configuration of the hydrogen atom is $1s^1$ meaning that it has one electron in the 1s orbital. The second electron in helium (He) can also occupy the 1s orbital. Its configuration is, therefore, $1s^2$. As mentioned above, the two electrons differ from each other with opposite spin, as can be seen from the orbital diagram. The third electron of lithium (Li) is not allowed in the 1s orbital because of Pauli exclusion principle. It, therefore, takes the next available choice, namely the 2s orbital. The electronic configuration of Li is $1s^2 2s^1$. The 2s orbital can accommodate one more electron. The configuration of beryllium (Be) atom is, therefore, $1s^2\ 2s^2$ (see Table 2.6, page 66 for the electronic configurations of elements). In the next six elements—boron (B, $1s^2 2s^2 2p^1$), carbon (C, $1s^2 2s^2 2p^2$), nitrogen (N, $1s^2 2s^2 2p^3$), oxygen (O, $1s^2 2s^2 2p^4$), fluorine (F, $1s^2 2s^2 2p^5$) and neon (Ne, $1s^2 2s^2 2p^6$), the 2p orbitals get progressively filled. This process is completed with the neon atom. The orbital picture of these elements can be represented as follows : The electronic configuration of the elements sodium (Na, $1s^2 2s^2 2p^6 3s^1$) to argon (Ar, $1s^2 2s^2 2p^6 3s^2 3p^6$), follow exactly the same pattern as the elements from lithium to neon with the difference that the 3s and 3p orbitals are getting filled now. This process can be simplified if we represent the total number of electrons in the first two shells by the name of element neon (Ne). The electronic configuration of the elements from sodium to Rationalised 2023-24 64 chemistry argon can be written as (Na, [Ne]$3s^1$) to (Ar, [Ne] $3s^2 3p^6$). The electrons in the completely filled shells are known as core electrons and the electrons that are added to the electronic shell with the highest principal quantum number are called valence electrons. For example, the electrons in Ne are the core electrons and the electrons from Na to Ar are the valence electrons. In potassium (K) and calcium (Ca), the 4s orbital, being lower in energy than the 3d orbitals, is occupied by one and two electrons respectively. A new pattern is followed beginning with scandium (Sc). The 3d orbital, being lower in energy than the 4p orbital, is filled first. Consequently, in the next ten elements, scandium (Sc), titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu) and zinc (Zn), the five 3d orbitals are progressively occupied. We may be puzzled by the fact that chromium and copper have five and ten electrons in 3d orbitals rather than four and nine as their position would have indicated with two-electrons in the 4s orbital. The reason is that fully filled orbitals and halffilled orbitals have extra stability (that is, lower energy). Thus $p^3$, $p^6$, $d^5$, $d^{10}$,$f^7$, $f^{14}$

etc. configurations, which are either half-filled or fully filled, are more stable. Chromium and copper therefore adopt the d5 and d10 configuration (Section 2.6.7)[caution: exceptions do exist] With the saturation of the 3d orbitals, the filling of the 4p orbital starts at gallium (Ga) and is complete at krypton (Kr). In the next eighteen elements from rubidium (Rb) to xenon (Xe), the pattern of filling the 5s, 4d and 5p orbitals are similar to that of 4s, 3d and 4p orbitals as discussed above. Then comes the turn of the 6s orbital. In caesium (Cs) and the barium (Ba), this orbital contains one and two electrons, respectively. Then from lanthanum (La) to mercury (Hg), the filling up of electrons takes place in 4f and 5d orbitals. After this, filling of 6p, then 7s and finally 5f and 6d orbitals takes place. The elements after uranium (U) are all short-lived and all of them are produced artificially. The electronic configurations of the known elements (as determined by spectroscopic methods) are tabulated in Table 2.6 (page 66). One may ask what is the utility of knowing the electron configuration? The modern approach to the chemistry, infact, depends almost entirely on electronic distribution to understand and explain chemical behaviour. For example, questions like why two or more atoms combine to form molecules, why some elements are metals while others are nonmetals, why elements like helium and argon are not reactive but elements like the halogens are reactive, find simple explanation from the electronic configuration. These questions have no answer in the Daltonian model of atom. A detailed understanding of the electronic structure of atom is, therefore, very essential for getting an insight into the various aspects of modern chemical knowledge. 2.6.6 Stability of Completely Filled and Half Filled Subshells The ground state electronic configuration of the atom of an element always corresponds to the state of the lowest total electronic energy. The electronic configurations of most of the atoms follow the basic rules given in Section 2.6.5. However, in certain elements such as Cu, or Cr, where the two subshells (4s and 3d) differ slightly in their energies, an electron shifts from a subshell of lower energy (4s) to a subshell of higher energy (3d), provided such a shift results in all orbitals of the subshell of higher energy getting either completely filled or half filled. The valence electronic configurations of Cr and Cu, therefore, are 3d5 4s1 and 3d10 4s1 respectively and not 3d4 4s2 and 3d9 4s2.It has been found that there is extra stability associated with these electronic configurations. Rationalised 2023-24 structure of atom 65 The completely filled and completely half-filled subshells are stable due to the following reasons: 1 . Symm e t r i ca l d i s t r ibu t ion o f electrons: It is well known that symmetry leads to stability. The completely filled or half filled subshells have symmetrical distribution of electrons in them and are therefore more stable. Electrons in the same subshell (here 3d) have equal energy but different spatial distribution. Consequently, their shielding of oneanother is relatively small and the electrons are more strongly attracted by the nucleus. 2. Exchange Energy : The stabilizing effect arises whenever two or more electrons with the same spin are present in the degenerate orbitals of a subshell. These electrons tend to exchange their positions and the energy released due to this exchange is called exchange energy. The number of exchanges that can take place is maximum when the subshell is either half filled or completely filled (Fig. 2.18). As a result the exchange energy is maximum and so is the stability. You may note that the exchange energy is at the basis of Hund's rule that electrons which enter orbitals of equal energy have parallel spins as far as possible. In other words, the extra stability of half-filled and completely filled subshell is due to: (i) relatively small shielding, (ii) smaller coulombic repulsion energy, and (iii) larger exchange energy. Details about the exchange energy will be dealt with in higher classes. Fig. 2.18 Possible exchange for a d5 configuration Causes of Stability of Completely Filled and Half-filled Subshells Rationalised 2023-24 66 chemistry Table 2.6 Electronic Configurations of the Elements * Elements with exceptional electronic configurations Rationalised 2023-24 structure of atom 67 ** Elements with atomic number 112 and above have been reported but not yet fully authenticated and named. Rationalised 2023-24 68 chemistry Summary Atoms are the building blocks of elements. They are the smallest parts of an element that chemically react. The first atomic theory, proposed by John Dalton in 1808,

regarded atom as the ultimate indivisible particle of matter. Towards the end of the nineteenth century, it was proved experimentally that atoms are divisible and consist of three fundamental particles: electrons, protons and neutrons. The discovery of sub-atomic particles led to the proposal of various atomic models to explain the structure of atom. Thomson in 1898 proposed that an atom consists of uniform sphere of positive electricity with electrons embedded into it. This model in which mass of the atom is considered to be evenly spread over the atom was proved wrong by Rutherford's famous alpha-particle scattering experiment in 1909. Rutherford concluded that atom is made of a tiny positively charged nucleus, at its centre with electrons revolving around it in circular orbits. Rutherford model, which resembles the solar system, was no doubt an improvement over Thomson model but it could not account for the stability of the atom i.e., why the electron does not fall into the nucleus. Further, it was also silent about the electronic structure of atoms i.e., about the distribution and relative energies of electrons around the nucleus. The difficulties of the Rutherford model were overcome by Niels Bohr in 1913 in his model of the hydrogen atom. Bohr postulated that electron moves around the nucleus in circular orbits. Only certain orbits can exist and each orbit corresponds to a specific energy. Bohr calculated the energy of electron in various orbits and for each orbit predicted the distance between the electron and nucleus. Bohr model, though offering a satisfactory model for explaining the spectra of the hydrogen atom, could not explain the spectra of multi-electron atoms. The reason for this was soon discovered. In Bohr model, an electron is regarded as a charged particle moving in a well defined circular orbit about the nucleus. The wave character of the electron is ignored in Bohr's theory. An orbit is a clearly defined path and this path can completely be defined only if both the exact position and the exact velocity of the electron at the same time are known. This is not possible according to the Heisenberg uncertainty principle. Bohr model of the hydrogen atom, therefore, not only ignores the dual behaviour of electron but also contradicts Heisenberg uncertainty principle. Erwin Schrödinger, in 1926, proposed an equation called Schrödinger equation to describe the electron distributions in space and the allowed energy levels in atoms. This equation incorporates de Broglie's concept of wave-particle duality and is consistent with Heisenberg uncertainty principle. When Schrödinger equation is solved for the electron in a hydrogen atom, the solution gives the possible energy states the electron can occupy [and the corresponding wave function(s) ($\psi$) (which in fact are the mathematical functions) of the electron associated with each energy state]. These quantized energy states and corresponding wave functions which are characterized by a set of three quantum numbers (principal quantum number n, azimuthal quantum number l and magnetic quantum number ml ) arise as a natural consequence in the solution of the Schrödinger equation. The restrictions on the values of these three quantum numbers also come naturally from this solution. The quantum mechanical model of the hydrogen atom successfully predicts all aspects of the hydrogen atom spectrum including some phenomena that could not be explained by the Bohr model. According to the quantum mechanical model of the atom, the electron distribution of an atom containing a number of electrons is divided into shells. The shells, in turn, are thought to consist of one or more subshells and subshells are assumed to be composed of one or more orbitals, which the electrons occupy. While for hydrogen and hydrogen like systems (such as He+, Li2+ etc.) all the orbitals within a given shell have same energy, the energy of the orbitals in a multi-electron atom depends upon the values of n and l: The lower the value of (n + l ) for an orbital, the lower is its energy. If two orbitals have the same (n + l ) value, the orbital with lower value of n has the lower energy. In an atom many such orbitals are Rationalised 2023-24 structure of atom 69 possible and electrons are filled in those orbitals in order of increasing energy in accordance with Pauli exclusion principle (no two electrons in an atom can have the same set of four quantum numbers) and Hund's rule of maximum multiplicity (pairing of electrons in the orbitals belonging to the same subshell does not take place until each orbital belonging to that subshell has got one electron each, i.e., is singly occupied). This forms the basis of the electronic structure of

atoms. EXERCISES 2.1 (i) Calculate the number of electrons which will together weigh one gram. (ii) Calculate the mass and charge of one mole of electrons. 2.2 (i) Calculate the total number of electrons present in one mole of methane. (ii) Find (a) the total number and (b) the total mass of neutrons in 7 mg of $^{14}C$. (Assume that mass of a neutron = $1.675 \times 10^{-27}$ kg). (iii) Find (a) the total number and (b) the total mass of protons in 34 mg of $NH_3$ at STP. Will the answer change if the temperature and pressure are changed ? 2.3 How many neutrons and protons are there in the following nuclei ? $^{13}_6C$, $^{16}_8O$, $^{24}_{12}Mg$, $^{56}_{26}Fe$, $^{88}_{38}Sr$ 2.4 Write the complete symbol for the atom with the given atomic number (Z) and atomic mass (A) (i) Z = 17, A = 35. (ii) Z = 92, A = 233. (iii) Z = 4, A = 9. 2.5 Yellow light emitted from a sodium lamp has a wavelength (λ) of 580 nm. Calculate the frequency (ν) and wavenumber ( ) of the yellow light. 2.6 Find energy of each of the photons which (i) correspond to light of frequency $3 \times 10^{15}$ Hz. (ii) have wavelength of 0.50 Å. 2.7 Calculate the wavelength, frequency and wavenumber of a light wave whose period is $2.0 \times 10^{-10}$ s. 2.8 What is the number of photons of light with a wavelength of 4000 pm that provide 1J of energy? 2.9 A photon of wavelength $4 \times 10^{-7}$ m strikes on metal surface, the work function of the metal being 2.13 eV. Calculate (i) the energy of the photon (eV), (ii) the kinetic energy of the emission, and (iii) the velocity of the photoelectron (1 eV= $1.6020 \times 10^{-19}$ J). 2.10 Electromagnetic radiation of wavelength 242 nm is just sufficient to ionise the sodium atom. Calculate the ionisation energy of sodium in kJ mol$^{-1}$. 2.11 A 25 watt bulb emits monochromatic yellow light of wavelength of 0.57μm. Calculate the rate of emission of quanta per second. 2.12 Electrons are emitted with zero velocity from a metal surface when it is exposed to radiation of wavelength 6800 Å. Calculate threshold frequency ($\nu_0$) and work function ($W_0$) of the metal. 2.13 What is the wavelength of light emitted when the electron in a hydrogen atom undergoes transition from an energy level with n = 4 to an energy level with n = 2? Rationalised 2023-24 70 chemistry 2.14 How much energy is required to ionise a H atom if the electron occupies n = 5 orbit? Compare your answer with the ionization enthalpy of H atom (energy required to remove the electron from n =1 orbit). 2.15 What is the maximum number of emission lines when the excited electron of a H atom in n = 6 drops to the ground state? 2.16 (i) The energy associated with the first orbit in the hydrogen atom is $-2.18 \times 10^{-18}$ J atom$^{-1}$. What is the energy associated with the fifth orbit? (ii) Calculate the radius of Bohr's fifth orbit for hydrogen atom. 2.17 Calculate the wavenumber for the longest wavelength transition in the Balmer series of atomic hydrogen. 2.18 What is the energy in joules, required to shift the electron of the hydrogen atom from the first Bohr orbit to the fifth Bohr orbit and what is the wavelength of the light emitted when the electron returns to the ground state? The ground state electron energy is $-2.18 \times 10^{-11}$ ergs. 2.19 The electron energy in hydrogen atom is given by $E_n = (-2.18 \times 10^{-18})/n^2$ J. Calculate the energy required to remove an electron completely from the n = 2 orbit. What is the longest wavelength of light in cm that can be used to cause this transition? 2.20 Calculate the wavelength of an electron moving with a velocity of $2.05 \times 10^7$ m s$^{-1}$. 2.21 The mass of an electron is $9.1 \times 10^{-31}$ kg. If its K.E. is $3.0 \times 10^{-25}$ J, calculate its wavelength. 2.22 Which of the following are isoelectronic species i.e., those having the same number of electrons? $Na^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$, $S^{2-}$, Ar. 2.23 (i) Write the electronic configurations of the following ions: (a) $H^-$ (b) $Na^+$ (c) $O^{2-}$ (d) $F^-$ (ii) What are the atomic numbers of elements whose outermost electrons are represented by (a) $3s^1$ (b) $2p^3$ and (c) $3p^5$ ? (iii) Which atoms are indicated by the following configurations ? (a) [He] $2s^1$ (b) [Ne] $3s^2 3p^3$ (c) [Ar] $4s^2 3d^1$. 2.24 What is the lowest value of n that allows g orbitals to exist? 2.25 An electron is in one of the 3d orbitals. Give the possible values of n, l and $m_l$ for this electron. 2.26 An atom of an element contains 29 electrons and 35 neutrons. Deduce (i) the number of protons and (ii) the electronic configuration of the element. 2.27 Give the number of electrons in the species 2.28 (i) An atomic orbital has n = 3. What are the possible values of l and $m_l$ ? (ii) List the quantum numbers ($m_l$ and l) of electrons for 3d orbital. (iii) Which of the following orbitals are possible? 1p, 2s, 2p and 3f 2.29 Using s, p, d notations, describe the orbital with the following quantum numbers.

(a) n=1, l=0; (b) n = 3; l=1 (c) n = 4; l =2; (d) n=4; l=3. 2.30 Explain, giving reasons, which of the following sets of quantum numbers are not possible. (a) n = 0, l = 0, ml = 0, ms = + ½ (b) n = 1, l = 0, ml = 0, ms = − ½ (c) n = 1, l = 1, ml = 0, ms = + ½ (d) n = 2, l = 1, ml = 0, ms = − ½ Rationalised 2023-24 structure of atom 71 (e) n = 3, l = 3, ml = –3, ms = + ½ (f) n = 3, l = 1, ml = 0, ms = + ½ 2.31 How many electrons in an atom may have the following quantum numbers? (a) n = 4, ms = − ½ (b) n = 3, l = 0 2.32 Show that the circumference of the Bohr orbit for the hydrogen atom is an integral multiple of the de Broglie wavelength associated with the electron revolving around the orbit. 2.33 What transition in the hydrogen spectrum would have the same wavelength as the Balmer transition n = 4 to n = 2 of He+ spectrum ? 2.34 Calculate the energy required for the process He+ (g) $\gamma$ He2+ (g) + e– The ionization energy for the H atom in the ground state is $2.18 \times 10^{-18}$ J atom$^{-1}$ 2.35 If the diameter of a carbon atom is 0.15 nm, calculate the number of carbon atoms which can be placed side by side in a straight line across length of scale of length 20 cm long. 2.36 $2 \times 10^{8}$ atoms of carbon are arranged side by side. Calculate the radius of carbon atom if the length of this arrangement is 2.4 cm. 2.37 The diameter of zinc atom is 2.6 Å. Calculate (a) radius of zinc atom in pm and (b) number of atoms present in a length of 1.6 cm if the zinc atoms are arranged side by side lengthwise. 2.38 A certain particle carries $2.5 \times 10^{-16}$C of static electric charge. Calculate the number of electrons present in it. 2.39 In Milikan's experiment, static electric charge on the oil drops has been obtained by shining X-rays. If the static electric charge on the oil drop is $-1.282 \times 10^{-18}$C, calculate the number of electrons present on it. 2.40 In Rutherford's experiment, generally the thin foil of heavy atoms, like gold, platinum etc. have been used to be bombarded by the α-particles. If the thin foil of light atoms like aluminium etc. is used, what difference would be observed from the above results ? 2.41 Symbols 35 79Br and 79Br can be written, whereas symbols 79 35Br and 35Br are not acceptable. Answer briefly. 2.42 An element with mass number 81 contains 31.7% more neutrons as compared to protons. Assign the atomic symbol. 2.43 An ion with mass number 37 possesses one unit of negative charge. If the ion conatins 11.1% more neutrons than the electrons, find the symbol of the ion. 2.44 An ion with mass number 56 contains 3 units of positive charge and 30.4% more neutrons than electrons. Assign the symbol to this ion. 2.45 Arrange the following type of radiations in increasing order of frequency: (a) radiation from microwave oven (b) amber light from traffic signal (c) radiation from FM radio (d) cosmic rays from outer space and (e) X-rays. 2.46 Nitrogen laser produces a radiation at a wavelength of 337.1 nm. If the number of photons emitted is $5.6 \times 10^{24}$, calculate the power of this laser. 2.47 Neon gas is generally used in the sign boards. If it emits strongly at 616 nm, calculate (a) the frequency of emission, (b) distance traveled by this radiation in 30 s (c) energy of quantum and (d) number of quanta present if it produces 2 J of energy. Rationalised 2023-24 72 chemistry 2.48 In astronomical observations, signals observed from the distant stars are generally weak. If the photon detector receives a total of $3.15 \times 10^{-18}$ J from the radiations of 600 nm, calculate the number of photons received by the detector. 2.49 Lifetimes of the molecules in the excited states are often measured by using pulsed radiation source of duration nearly in the nano second range. If the radiation source has the duration of 2 ns and the number of photons emitted during the pulse source is $2.5 \times 10^{15}$, calculate the energy of the source. 2.50 The longest wavelength doublet absorption transition is observed at 589 and 589.6 nm. Calcualte the frequency of each transition and energy difference between two excited states. 2.51 The work function for caesium atom is 1.9 eV. Calculate (a) the threshold wavelength and (b) the threshold frequency of the radiation. If the caesium element is irradiated with a wavelength 500 nm, calculate the kinetic energy and the velocity of the ejected photoelectron. 2.52 Following results are observed when sodium metal is irradiated with different wavelengths. Calculate (a) threshold wavelength and, (b) Planck's constant. λ (nm) 500 450 400 v × 10–5 (cm s–1) 2.55 4.35 5.35 2.53 The ejection of the photoelectron from the silver metal in the photoelectric effect experiment can be stopped by applying the voltage of 0.35 V when the radiation 256.7 nm is used. Calculate the work function for

silver metal. 2.54 If the photon of the wavelength 150 pm strikes an atom and one of tis inner bound electrons is ejected out with a velocity of $1.5 \times 10^7$ m s–1, calculate the energy with which it is bound to the nucleus. 2.55 Emission transitions in the Paschen series end at orbit n = 3 and start from orbit n and can be represeted as $v = 3.29 \times 10^{15}$ (Hz) $[1/3^2 – 1/n^2]$ Calculate the value of n if the transition is observed at 1285 nm. Find the region of the spectrum. 2.56 Calculate the wavelength for the emission transition if it starts from the orbit having radius 1.3225 nm and ends at 211.6 pm. Name the series to which this transition belongs and the region of the spectrum. 2.57 Dual behaviour of matter proposed by de Broglie led to the discovery of electron microscope often used for the highly magnified images of biological molecules and other type of material. If the velocity of the electron in this microscope is $1.6 \times 10^6$ ms–1, calculate de Broglie wavelength associated with this electron. 2.58 Similar to electron diffraction, neutron diffraction microscope is also used for the determination of the structure of molecules. If the wavelength used here is 800 pm, calculate the characteristic velocity associated with the neutron. 2.59 If the velocity of the electron in Bohr's first orbit is $2.19 \times 10^6$ ms–1, calculate the de Broglie wavelength associated with it. 2.60 The velocity associated with a proton moving in a potential difference of 1000 V is $4.37 \times 10^5$ ms–1. If the hockey ball of mass 0.1 kg is moving with this velocity, calcualte the wavelength associated with this velocity. 2.61 If the position of the electron is measured within an accuracy of + 0.002 nm, calculate the uncertainty in the momentum of the electron. Suppose the momentum of the electron is h/4πm × 0.05 nm, is there any problem in defining this value. 2.62 The quantum numbers of six electrons are given below. Arrange them in order of increasing energies. If any of these combination(s) has/have the same energy lists: 1. n = 4, l = 2, ml = –2 , ms = –1/2 2. n = 3, l = 2, ml = 1 , ms = +1/2 Rationalised 2023-24 structure of atom 73 3. n = 4, l = 1, ml = 0 , ms = +1/2 4. n = 3, l = 2, ml = –2 , ms = –1/2 5. n = 3, l = 1, ml = –1 , ms = +1/2 6. n = 4, l = 1, ml = 0 , ms = +1/2 2.63 The bromine atom possesses 35 electrons. It contains 6 electrons in 2p orbital, 6 electrons in 3p orbital and 5 electron in 4p orbital. Which of these electron experiences the lowest effective nuclear charge ? 2.64 Among the following pairs of orbitals which orbital will experience the larger effective nuclear charge? (i) 2s and 3s, (ii) 4d and 4f, (iii) 3d and 3p. 2.65 The unpaired electrons in Al and Si are present in 3p orbital. Which electrons will experience more effective nuclear charge from the nucleus ? 2.66 Indicate the number of unpaired electrons in : (a) P, (b) Si, (c) Cr, (d) Fe and (e) Kr. 2.67 (a) How many subshells are associated with n = 4 ? (b) How many electrons will be present in the subshells having ms value of – 1/2 for n = 4 ? Rationalised 2023-24The Periodic Table is arguably the most important concept in chemistry, both in principle and in practice. It is the everyday support for students, it suggests new avenues of research to professionals, and it provides a succinct organization of the whole of chemistry. It is a remarkable demonstration of the fact that the chemical elements are not a random cluster of entities but instead display trends and lie together in families. An awareness of the Periodic Table is essential to anyone who wishes to disentangle the world and see how it is built up from the fundamental building blocks of the chemistry, the chemical elements. Glenn T. Seaborg Unit 3 Classification of Elements and Periodicity in Properties After studying this Unit, you will be able to • appreciate how the concept of grouping elements in accordance to their properties led to the development of Periodic Table. • understand the Periodic Law; • understand the significance of atomic number and electronic configuration as the basis for periodic classification; • n a m e t h e e l e m e n t s w i t h Z >100 according to IUPAC nomenclature; • classify elements into s, p, d, f blocks and learn their main characteristics; • recognise the periodic trends in physical and chemical properties of elements; • compare the reactivity of elements and correlate it with their occurrence in nature; • explain the relationship between ionization enthalpy and metallic character; • use scientific vocabulary appropriately to communicate ideas related to certain important properties of atoms e.g., atomic/ionic radii, ionization enthalpy, electron gain enthalpy, electronegativity, valence of elements. In this Unit, we will study the historical development of the Periodic Table as it stands

today and the Modern Periodic Law. We will also learn how the periodic classification follows as a logical consequence of the electronic configuration of atoms. Finally, we shall examine some of the periodic trends in the physical and chemical properties of the elements. 3.1 WHY DO WE NEED TO CLASSIFY ELEMENTS ? We know by now that the elements are the basic units of all types of matter. In 1800, only 31 elements were known. By 1865, the number of identified elements had more than doubled to 63. At present 114 elements are known. Of them, the recently discovered elements are man-made. Efforts to synthesise new elements are continuing. With such a large number of elements it is very difficult to study individually the chemistry of all these elements and their innumerable compounds individually. To ease out this problem, scientists searched for a systematic way to organise their knowledge by classifying the elements. Not only that it would rationalize known chemical facts about elements, but even predict new ones for undertaking further study. Rationalised 2023-24 Classification of Elements and Periodicity in Properties 75 3.2 GENESIS OF PERIODIC CLASSIFICATION Classification of elements into groups and development of Periodic Law and Periodic Table are the consequences of systematising the knowledge gained by a number of scientists through their observations and experiments. The German chemist, Johann Dobereiner in early 1800's was the first to consider the idea of trends among properties of elements. By 1829 he noted a similarity among the physical and chemical properties of several groups of three elements (Triads). In each case, he noticed that the middle element of each of the Triads had an atomic weight about half way between the atomic weights of the other two (Table 3.1). Also the properties of the middle element were in between those of the other two members. Since Dobereiner's the periodic recurrence of properties. This also did not attract much attention. The English chemist, John Alexander Newlands in 1865 profounded the Law of Octaves. He arranged the elements in increasing order of their atomic weights and noted that every eighth element had properties similar to the first element (Table 3.2). The relationship was just like every eighth note that resembles the first in octaves of music. Newlands's Law of Octaves seemed to be true only for elements up to calcium. Although his idea was not widely accepted at that time, he, for his work, was later awarded Davy Medal in 1887 by the Royal Society, London. The Periodic Law, as we know it today owes its development to the Russian chemist, Dmitri Mendeleev (1834-1907) and the German chemist, Lothar Meyer (1830-1895). Table 3.1 Dobereiner's Triads Element Atomic weight Element Atomic weight Element Atomic weight Li Na K 7 23 39 Ca Sr Ba 40 88 137 Cl Br I 35.5 80 127 Table 3.2 Newlands' Octaves Element Li Be B C N O F At. wt. 7 9 11 12 14 16 19 Element Na Mg Al Si P S Cl At. wt. 23 24 27 29 31 32 35.5 Element K Ca At. wt. 39 40 relationship, referred to as the Law of Triads, seemed to work only for a few elements, it was dismissed as coincidence. The next reported attempt to classify elements was made by a French geologist, A.E.B. de Chancourtois in 1862. He arranged the then known elements in order of increasing atomic weights and made a cylindrical table of elements to display Working independently, both the chemists in 1869 proposed that on arranging elements in the increasing order of their atomic weights, similarities appear in physical and chemical properties at regular intervals. Lothar Meyer plotted the physical properties such as atomic volume, melting point and boiling point against atomic weight and obtained Rationalised 2023-24 76 chemistry a periodically repeated pattern. Unlike Newlands, Lothar Meyer observed a change in length of that repeating pattern. By 1868, Lothar Meyer had developed a table of the elements that closely resembles the Modern Periodic Table. However, his work was not published until after the work of Dmitri Mendeleev, the scientist who is generally credited with the development of the Modern Periodic Table. While Dobereiner initiated the study of periodic relationship, it was Mendeleev who was responsible for publishing the Periodic Law for the first time. It states as follows : The properties of the elements are a periodic function of their atomic weights. Mendeleev arranged elements in horizontal rows and vertical columns of a table in order of their increasing atomic weights in such a way that the elements with similar properties occupied the same vertical column

or group. Mendeleev's system of classifying elements was more elaborate than that of Lothar Meyer's. He fully recognized the significance of periodicity and used broader range of physical and chemical properties to classify the elements. In particular, Mendeleev relied on the similarities in the empirical formulas and properties of the compounds formed by the elements. He realized that some of the elements did not fit in with his scheme of classification if the order of atomic weight was strictly followed. He ignored the order of atomic weights, thinking that the atomic measurements might be incorrect, and placed the elements with similar properties together. For example, iodine with lower atomic weight than that of tellurium (Group VI) was placed in Group VII along with fluorine, chlorine, bromine because of similarities in properties (Fig. 3.1). At the same time, keeping his primary aim of arranging the elements of similar properties in the same group, he proposed that some of the elements were still undiscovered and, therefore, left several gaps in the table. For example, both gallium and germanium were unknown at the time Mendeleev published his Periodic Table. He left the gap under aluminium and a gap under silicon, and called these elements Eka-Aluminium and Eka-Silicon. Mendeleev predicted not only the existence of gallium and germanium, but also described some of their general physical properties. These elements were discovered later. Some of the properties predicted by Mendeleev for these elements and those found experimentally are listed in Table 3.3. The boldness of Mendeleev's quantitative predictions and their eventual success made him and his Periodic Table famous. Mendeleev's Periodic Table published in 1905 is shown in Fig. 3.1.

Table 3.3 Mendeleev's Predictions for the Elements Eka-aluminium (Gallium) and Eka-silicon (Germanium)

| Property | Eka-aluminium (predicted) | Gallium (found) | Eka-silicon (predicted) | Germanium (found) |
|---|---|---|---|---|
| Atomic weight | 68 | 70 | 72 | 72.6 |
| Density/(g/cm3) | 5.9 | 5.94 | 5.5 | 5.36 |
| Melting point/K | Low | 302.93 | High | 1231 |
| Formula of oxide | $E_2O_3$ | $Ga_2O_3$ | $EO_2$ | $GeO_2$ |
| Formula of chloride | $ECl_3$ | $GaCl_3$ | $ECl_4$ | $GeCl_4$ |

Classifi cation of El e m ents and P eriodi city in Properti e s 77 PERIODIC SYSTEM OF THE ELEMENTS IN GROUPS AND SERIES Fig. 3.1 Mendeleev's Periodic Table published earlier

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## 3.3 MODERN PERIODIC LAW AND THE PRESENT FORM OF THE PERIODIC TABLE

We must bear in mind that when Mendeleev developed his Periodic Table, chemists knew nothing about the internal structure of atom. However, the beginning of the 20th century witnessed profound developments in theories about sub-atomic particles. In 1913, the English physicist, Henry Moseley observed regularities in the characteristic X-ray spectra of the elements. A plot of (where is frequency of X-rays emitted) against atomic number (Z) gave a straight line and not the plot of vs atomic mass. He thereby showed that the atomic number is a more fundamental property of an element than its atomic mass. Mendeleev's Periodic Law was, therefore, accordingly modified. This is known as the Modern Periodic Law and can be stated as : The physical and chemical properties of the elements are periodic functions of their atomic numbers. The Periodic Law revealed important analogies among the 94 naturally occurring elements (neptunium and plutonium like actinium and protoactinium are also found in pitch blende – an ore of uranium). It stimulated renewed interest in Inorganic Chemistry and has carried into the present with the creation of artificially produced short-lived elements. You may recall that the atomic number is equal to the nuclear charge (i.e., number of protons) or the number of electrons in a neutral atom. It is then easy to visualize the significance of quantum numbers and electronic configurations in periodicity of elements. In fact, it is now recognized that the Periodic Law is essentially the consequence of the periodic variation in electronic configurations, which indeed determine the physical and chemical properties of elements and their compounds. Numerous forms of Periodic Table have been devised from time to time. Some forms emphasise chemical reactions and valence, whereas others stress the electronic configuration of elements. A modern version, the so-called "long form" of the Periodic Table of the elements (Fig. 3.2), is the most convenient and widely used. The horizontal rows (which Mendeleev called series) are called periods and the vertical columns, groups. Elements having similar outer electronic configurations in their atoms are arranged in vertical

columns, referred to as groups or families. According to the recommendation of International Union of Pure and Applied Chemistry (IUPAC), the groups are numbered from 1 to 18 replacing the older notation of groups IA … VIIA, VIII, IB … VIIB and 0. There are altogether seven periods. The period number corresponds to the highest principal quantum number (n) of the elements in the period. The first period contains 2 elements. The subsequent periods consists of 8, 8, 18, 18 and 32 elements, respectively. The seventh period is incomplete and like the sixth period would have a theoretical maximum (on the basis of quantum numbers) of 32 elements. In this form of the Periodic Table, 14 elements of both sixth and seventh periods (lanthanoids and actinoids, respectively) are placed in separate panels at the bottom*. 3.4 NOMENCLATURE OF ELEMENTS WITH ATOMIC NUMBERS > 100 The naming of the new elements had been traditionally the privilege of the discoverer (or discoverers) and the suggested name was ratified by the IUPAC. In recent years this has led to some controversy. The new elements with very high atomic numbers are so unstable that only minute quantities, sometimes only * Glenn T. Seaborg's work in the middle of the 20th century starting with the discovery of plutonium in 1940, followed by those of all the transuranium elements from 94 to 102 led to reconfiguration of the periodic table placing the actinoids below the lanthanoids. In 1951, Seaborg was awarded the Nobel Prize in chemistry for his work. Element 106 has been named Seaborgium (Sg) in his honour. Rationalised 2023-24 Classifi cation of El e m ents and P eriodi city in Properti e s 79 Fig. 3.2 Long form of the Periodic Table of the Elements with their atomic numbers and ground state outer electronic configurations. The groups are numbered 1-18 in accordance with the 1984 IUPAC recommendations. This notation replaces the old numbering scheme of IA–VIIA, VIII, IB–VIIB and 0 for the elements. III A IV A V A VI A VII A ← VIII → I B II B IA IIA III B IV B V B VI B VII B 0 Rationalised 2023-24 80 chemistry a few atoms of them are obtained. Their synthesis and characterisation, therefore, require highly sophisticated costly equipment and laboratory. Such work is carried out with competitive spirit only in some laboratories in the world. Scientists, before collecting the reliable data on the new element, at times get tempted to claim for its discovery. For example, both American and Soviet scientists claimed credit for discovering element 104. The Americans named it Rutherfordium whereas Soviets named it Kurchatovium. To avoid such problems, the IUPAC has made recommendation that until a new element's discovery is proved, and its name is officially recognised, a systematic nomenclature be derived directly from the atomic number of the element using the numerical roots for 0 and numbers 1-9. These are shown in Table 3.4. The roots are put together in order of digits which make up the atomic number and "ium" is added at the end. The IUPAC names for elements with Z above 100 are shown in Table 3.5. Table 3.5 Nomenclature of Elements with Atomic Number Above 100 Atomic Number Name according to IUPAC nomenclature Symbol IUPAC Official Name IUPAC Symbol 101 102 103 104 105 106 107 108 109 110 111 112 113 114 115 116 117 118 Unnilunium Unnilbium Unniltrium Unnilquadium Unnilpentium Unnilhexium Unnilseptium Unniloctium Unnilennium Ununnillium Unununnium Ununbium Ununtrium Ununquadium Ununpentium Ununhexium Ununseptium Ununoctium Unu Unb Unt Unq Unp Unh Uns Uno Une Uun Uuu Uub Uut Uuq Uup Uuh Uus Uuo Mendelevium Nobelium Lawrencium Rutherfordium Dubnium Seaborgium Bohrium Hassium Meitnerium Darmstadtium Rontgenium Copernicium Nihonium Flerovium Moscovium Livermorium Tennessine Oganesson Md No Lr Rf Db Sg Bh Hs Mt Ds Rg Cn Nh Fl Mc Lv Ts Og Table 3.4 Notation for IUPAC Nomenclature of Elements Digit Name Abbreviation 0 1 2 3 4 5 6 7 8 9 nil un bi tri quad pent hex sept oct enn n u b t q p h s o e Rationalised 2023-24 Classification of Elements and Periodicity in Properties 81 Thus, the new element first gets a temporary name, with symbol consisting of three letters. Later permanent name and symbol are given by a vote of IUPAC representatives from each country. The permanent name might reflect the country (or state of the country) in which the element was discovered, or pay tribute to a notable scientist. As of now, elements with atomic numbers up to 118 have been discovered. Official names of all elements have been announced by IUPAC. Problem 3.1 What would

be the IUPAC name and symbol for the element with atomic number 120? Solution From Table 3.4, the roots for 1, 2 and 0 are un, bi and nil, respectively. Hence, the symbol and the name respectively are Ubn and unbinilium.

## 3.5 ELECTRONIC CONFIGURATIONS OF ELEMENTS AND THE PERIODIC TABLE

In the preceding unit we have learnt that an electron in an atom is characterised by a set of four quantum numbers, and the principal quantum number ($n$) defines the main energy level known as shell. We have also studied about the filling of electrons into different subshells, also referred to as orbitals (s, p, d, f) in an atom. The distribution of electrons into orbitals of an atom is called its electronic configuration. An element's location in the Periodic Table reflects the quantum numbers of the last orbital filled. In this section we will observe a direct connection between the electronic configurations of the elements and the long form of the Periodic Table.

(a) Electronic Configurations in Periods The period indicates the value of n for the outermost or valence shell. In other words, successive period in the Periodic Table is associated with the filling of the next higher principal energy level ($n = 1$, $n = 2$, etc.). It can be readily seen that the number of elements in each period is twice the number of atomic orbitals available in the energy level that is being filled. The first period ($n = 1$) starts with the filling of the lowest level ($1s$) and therefore has two elements — hydrogen ($1s^1$) and helium ($1s^2$) when the first shell (K) is completed. The second period ($n = 2$) starts with lithium and the third electron enters the 2s orbital. The next element, beryllium has four electrons and has the electronic configuration $1s^2 2s^2$. Starting from the next element boron, the 2p orbitals are filled with electrons when the L shell is completed at neon ($2s^2 2p^6$). Thus there are 8 elements in the second period. The third period ($n = 3$) begins at sodium, and the added electron enters a 3s orbital. Successive filling of 3s and 3p orbitals gives rise to the third period of 8 elements from sodium to argon. The fourth period ($n = 4$) starts at potassium, and the added electrons fill up the 4s orbital. Now you may note that before the 4p orbital is filled, filling up of 3d orbitals becomes energetically favourable and we come across the so called 3d transition series of elements. This starts from scandium ($Z = 21$) which has the electronic configuration $3d^1 4s^2$. The 3d orbitals are filled at zinc ($Z=30$) with electronic configuration $3d^{10} 4s^2$. The fourth period ends at krypton with the filling up of the 4p orbitals. Altogether we have 18 elements in this fourth period. The fifth period ($n = 5$) beginning with rubidium is similar to the fourth period and contains the 4d transition series starting at yttrium ($Z = 39$). This period ends at xenon with the filling up of the 5p orbitals. The sixth period ($n = 6$) contains 32 elements and successive electrons enter 6s, 4f, 5d and 6p orbitals, in the order — filling up of the 4f orbitals begins with cerium ($Z = 58$) and ends at lutetium ($Z = 71$) to give the 4f-inner transition series which is called the lanthanoid series. The seventh period ($n = 7$) is similar to the sixth period with the successive filling up of the 7s, 5f, 6d and 7p orbitals and includes most of the man-made radioactive elements. This period will end at the element with atomic number 118 which would belong to the noble gas family. Filling up of the 5f orbitals after Rationalised 2023-24 82 chemistry actinium ($Z = 89$) gives the 5f-inner transition series known as the actinoid series. The 4fand 5f-inner transition series of elements are placed separately in the Periodic Table to maintain its structure and to preserve the principle of classification by keeping elements with similar properties in a single column. Problem 3.2 How would you justify the presence of 18 elements in the 5th period of the Periodic Table? Solution When $n = 5$, $l = 0, 1, 2, 3$. The order in which the energy of the available orbitals 4d, 5s and 5p increases is $5s < 4d < 5p$. The total number of orbitals available are 9. The maximum number of electrons that can be accommodated is 18; and therefore 18 elements are there in the 5th period.

(b) Groupwise Electronic Configurations Elements in the same vertical column or group have similar valence shell electronic configurations, the same number of electrons in the outer orbitals, and similar properties. For example, the Group 1 elements (alkali metals) all have $ns^1$ valence shell electronic configuration as shown below. a theoretical foundation for the periodic classification.The elements ina vertical column of the Periodic Table constitute a group or family and exhibit similar chemical behaviour. This similarity arises because these elements have the

same number and same distribution of electrons in their outermost orbitals. We can classify the elements into four blocks viz., s-block, p-block, d-block and f-block depending on the type of atomic orbitals that are being filled withelectrons. This is illustrated in Fig. 3.3. We notice two exceptions to this categorisation. Strictly, helium belongs to the s-block but its positioning in the p-block along with other group 18 elements is justified because it has a completely filled valence shell ($1s^2$) and as a result, exhibits properties characteristic of other noble gases. The other exception is hydrogen. It has only one s-electron and hence can be placed in group 1 (alkali metals). It can also gain an electron to achieve a noble gas arrangement and hence it can behave similar to a group 17 (halogen family) elements. Because it is a special case, we shall place hydrogen separately at the top of the Periodic Table as shown in Fig. 3.2 and Fig. 3.3. We will briefly discuss the salient features of the four types of elements marked in the Periodic Table. More about these elements Thus it can be seen that the properties of an element have periodic dependence upon its atomic number and not on relative atomic mass. 3.6 ELECTRONIC CONFIGURATIONS AND TY P E S OF E L E M E NTS: s-, p-, d-, f- BLOCKS The aufbau (build up) principle and the electronic configuration of atoms provide will be discussed later. During the description of their features certain terminology has been used which has been classified in section 3.7. 3.6.1 The s-Block Elements The elements of Group 1 (alkali metals) and Group 2 (alkaline earth metals) which have $ns^1$ and $ns^2$ outermost electronic configuration belong to the s-Block Elements. They are all Atomic number Symbol Electronic configuration 3 11 19 37 55 87 Li Na K Rb Cs Fr $1s^2 2s^1$ (or) [He]$2s^1$ $1s^2 2s^2 2p^6 3s^1$ (or) [Ne]$3s^1$ $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ (or) [Ar]$4s^1$ $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^1$ (or) [Kr]$5s^1$ $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 6s^1$ (or) [Xe]$6s^1$ [Rn]$7s^1$ Rationalised 2023-24 Classifi cation of El e m ents and P eriodi city in Properti e s 83 Nh Mc Ts Og Fig. 3.3 The types of elements in the Periodic Table based on the orbitals that are being filled. Also shown is the broad division of elements into METALS ( ), NON-METALS ( ) and METALLOIDS ( ). Rationalised 2023-24 84 chemistry reactive metals with low ionization enthalpies. They lose the outermost electron(s) readily to form 1+ ion (in the case of alkali metals) or 2+ ion (in the case of alkaline earth metals). The metallic character and the reactivity increase as we go down the group. Because of high reactivity they are never found pure in nature. The compounds of the s-block elements, with the exception of those of lithium and beryllium are predominantly ionic. 3.6.2 The p-Block Elements The p-Block Elements comprise those belonging to Group 13 to 18 and these together with the s-Block Elements are called the Representative Elements or Main Group Elements. The outermost electronic configuration varies from $ns^2 np^1$ to $ns^2 np^6$ in each period. At the end of each period is a noble gas element with a closed valence shell $ns^2 np^6$ configuration. All the orbitals in the valence shell of the noble gases are completely filled by electrons and it is very difficult to alter this stable arrangement by the addition or removal of electrons. The noble gases thus exhibit very low chemical reactivity. Preceding the noble gas family are two chemically important groups of nonmetals. They are the halogens (Group 17) and the chalcogens (Group 16). These two groups of elements have highly negative electron gain enthalpies and readily add one or two electrons respectively to attain the stable noble gas configuration. The non-metallic character increases as we move from left to right across a period and metallic character increases as we go down the group. 3.6.3 The d-Block Elements (Transition Elements) These are the elements of Group 3 to 12 in the centre of the Periodic Table. These are characterised by the filling of inner d orbitals by electrons and are therefore referred to as d-Block Elements. These elements have the general outer electronic configuration $(n-1)d^{1-10} ns^{0-2}$ except for Pd where its electronic configuration is $4d^{10} 5s^0$.. They are all metals. They mostly form coloured ions, exhibit variable valence (oxidation states), paramagnetism and oftenly used as catalysts. However, Zn, Cd and Hg which have the electronic configuration, $(n-1)d^{10} ns^2$ do not show most of the properties of transition elements. In a way, transition metals form a bridge between the chemically active metals of s-block elements and the less active elements of Groups 13 and 14 and thus take their familiar name "Transition Elements".

3.6.4 The f-Block Elements (Inner-Transition Elements) The two rows of elements at the bottom of the Periodic Table, called the Lanthanoids, Ce(Z = 58) – Lu(Z = 71) and Actinoids, Th(Z = 90) – Lr (Z = 103) are characterised by the outer electronic configuration $(n-2)f^{1-14} (n-1)d^{0-1}ns^2$. The last electron added to each element is filled in f-orbital. These two series of elements are hence called the InnerTransition Elements (f-Block Elements). They are all metals. Within each series, the properties of the elements are quite similar. The chemistry of the early actinoids is more complicated than the corresponding lanthanoids, due to the large number of oxidation states possible for these actinoid elements. Actinoid elements are radioactive. Many of the actinoid elements have been made only in nanogram quantities or even less by nuclear reactions and their chemistry is not fully studied. The elements after uranium are called Transuranium Elements. Problem 3.3 The elements Z = 117 and 120 have not yet been discovered. In which family/group would you place these elements and also give the electronic configuration in each case. Solution We see from Fig. 3.2, that element with Z = 117, would belong to the halogen family (Group 17) and the electronic configuration would be [Rn] $5f^{14}6d^{10}7s^27p^5$. The element with Z = 120, will be placed in Group 2 (alkaline earth metals), and will have the electronic configuration [Uuo]$8s^2$. Rationalised 2023-24 Classification of Elements and Periodicity in Properties 85 3.6.5 Metals, Non-metals and Metalloids In addition to displaying the classification of elements into s-, p-, d-, and f-blocks, Fig. 3.3 shows another broad classification of elements based on their properties. The elements can be divided into Metals and Non-Metals. Metals comprise more than 78% of all known elements and appear on the left side of the Periodic Table. Metals are usually solids at room temperature [mercury is an exception; gallium and caesium also have very low melting points (303K and 302K, respectively)]. Metals usually have high melting and boiling points. They are good conductors of heat and electricity. They are malleable (can be flattened into thin sheets by hammering) and ductile (can be drawn into wires). In contrast, non-metals are located at the top right hand side of the Periodic Table. In fact, in a horizontal row, the property of elements change from metallic on the left to non-metallic on the right. Non-metals are usually solids or gases at room temperature with low melting and boiling points (boron and carbon are exceptions). They are poor conductors of heat and electricity. Most nonmetallic solids are brittle and are neither malleable nor ductile. The elements become more metallic as we go down a group; the non-metallic character increases as one goes from left to right across the Periodic Table. The change from metallic to non-metallic character is not abrupt as shown by the thick zig-zag line in Fig. 3.3. The elements (e.g., silicon, germanium, arsenic, antimony and tellurium) bordering this line and running diagonally across the Periodic Table show properties that are characteristic of both metals and non-metals. These elements are called Semi-metals or Metalloids. Problem 3.4 Considering the atomic number and position in the periodic table, arrange the following elements in the increasing order of metallic character : Si, Be, Mg, Na, P. Solution Metallic character increases down a group and decreases along a period as we move from left to right. Hence the order of increasing metallic character is: P < Si < Be < Mg < Na. 3.7 PERIODIC TRENDS IN PROPERTIES OF ELEMENTS There are many observable patterns in the physical and chemical properties of elements as we descend in a group or move across a period in the Periodic Table. For example, within a period, chemical reactivity tends to be high in Group 1 metals, lower in elements towards the middle of the table, and increases to a maximum in the Group 17 non-metals. Likewise within a group of representative metals (say alkali metals) reactivity increases on moving down the group, whereas within a group of non-metals (say halogens), reactivity decreases down the group. But why do the properties of elements follow these trends? And how can we explain periodicity? To answer these questions, we must look into the theories of atomic structure and properties of the atom. In this section we shall discuss the periodic trends in certain physical and chemical properties and try to explain them in terms of number of electrons and energy levels. 3.7.1 Trends in Physical Properties There are numerous physical properties of elements such as melting and boiling points, heats of

fusion and vaporization, energy of atomization, etc. which show periodic variations. However, we shall discuss the periodic trends with respect to atomic and ionic radii, ionization enthalpy, electron gain enthalpy and electronegativity. (a) Atomic Radius You can very well imagine that finding the size of an atom is a lot more complicated than measuring the radius of a ball. Do you know why? Firstly, because the size of an atom (~ 1.2 Å i.e., $1.2 \times 10^{-10}$ m in radius) is very small. Secondly, since the electron cloud surrounding the atom does not have a sharp boundary, the determination of the atomic size cannot be precise. In other words, there is no practical way by which the size of an individual atom can be measured. However, an estimate of the atomic size can be made by knowing the distance between the atoms in the combined state. One practical approach to estimate the size of an atom of a non-metallic element is to measure the distance between two atoms when they are bound together by a single bond in a covalent molecule and from this value, the "Covalent Radius" of the element can be calculated. For example, the bond distance in the chlorine molecule ($Cl_2$) is 198 pm and half this distance (99 pm), is taken as the atomic radius of chlorine. For metals, we define the term "Metallic Radius" which is taken as half the internuclear distance separating the metal cores in the metallic crystal. For example, the distance between two adjacent copper atoms in solid copper is 256 pm; hence the metallic radius of copper is assigned a value of 128 pm. For simplicity, in this book, we use the term Atomic Radius to refer to both covalent or metallic radius depending on whether the element is a non-metal or a metal. Atomic radii can be measured by X-ray or other spectroscopic methods. The atomic radii of a few elements are listed in Table 3.6. Two trends are obvious. We can explain these trends in terms of nuclear charge and energy level. The atomic size generally decreases across a period as illustrated in Fig. 3.4(a) for the elements of the second period. It is because within the period the outer electrons are in the same valence shell and the effective nuclear charge increases as the atomic number increases resulting in the increased attraction of electrons to the nucleus. Within a family or vertical column of the periodic table, the atomic radius increases regularly with atomic number as illustrated in Fig. 3.4(b). For alkali metals and halogens, as we descend the groups, the principal quantum number (n) increases and the valence electrons are farther from the nucleus. This happens because the inner energy levels are filled with electrons, which serve to shield the outer electrons from the pull of the nucleus. Consequently the size of the atom increases as reflected in the atomic radii. Note that the atomic radii of noble gases are not considered here. Being monoatomic, their (non-bonded radii) values are very large. In fact radii of noble gases should be compared not with the covalent radii but with the van der Waals radii of other elements.

Table 3.6(a) Atomic Radii/pm Across the Periods

| Atom (Period II) | Li | Be | B | C | N | O | F |
|---|---|---|---|---|---|---|---|
| Atomic radius | 152 | 111 | 88 | 77 | 74 | 66 | 64 |
| Atom (Period III) | Na | Mg | Al | Si | P | S | Cl |
| Atomic radius | 186 | 160 | 143 | 117 | 110 | 104 | 99 |

Table 3.6(b) Atomic Radii/pm Down a Family

| Atom (Group I) | Atomic Radius | Atom (Group 17) | Atomic Radius |
|---|---|---|---|
| Li | 152 | F | 64 |
| Na | 186 | Cl | 99 |
| K | 231 | Br | 114 |
| Rb | 244 | I | 133 |
| Cs | 262 | At | 140 |

(b) Ionic Radius The removal of an electron from an atom results in the formation of a cation, whereas gain of an electron leads to an anion. The ionic radii can be estimated by measuring the distances between cations and anions in ionic crystals. In general, the ionic radii of elements exhibit the same trend as the atomic radii. A cation is smaller than its parent atom because it has fewer electrons while its nuclear charge remains the same. The size of an anion will be larger than that of the parent atom because the addition of one or more electrons would result in increased repulsion among the electrons and a decrease in effective nuclear charge. For example, the ionic radius of fluoride ion ($F^-$) is 136 pm whereas the atomic radius of fluorine is only 64 pm. On the other hand, the atomic radius of sodium is 186 pm compared to the ionic radius of 95 pm for $Na^+$. When we find some atoms and ions which contain the same number of electrons, we call them isoelectronic species*. For example, $O^{2-}$, $F^-$, $Na^+$ and $Mg^{2+}$ have the same number of electrons (10). Their radii would be different because of their different nuclear charges. The Fig. 3.4 (a)

Variation of atomic radius with atomic number across the second period Fig. 3.4 (b) Variation of atomic radius with atomic number for alkali metals and halogens cation with the greater positive charge will have a smaller radius because of the greater attraction of the electrons to the nucleus. Anion with the greater negative charge will have the larger radius. In this case, the net repulsion of the electrons will outweigh the nuclear charge and the ion will expand in size. Problem 3.5 Which of the following species will have the largest and the smallest size? Mg, Mg2+, Al, Al3+. Solution Atomic radii decrease across a period. Cations are smaller than their parent atoms. Among isoelectronic species, the one with the larger positive nuclear charge will have a smaller radius. Hence the largest species is Mg; the smallest one is Al3+. (c) Ionization Enthalpy A quantitative measure of the tendency of an element to lose electron is given by its Ionization Enthalpy. It represents the energy required to remove an electron from an isolated gaseous atom (X) in its ground state. * Two or more species with same number of atoms, same number of valence electrons and same structure, regardless of the nature of elements involved. Rationalised 2023-24 88 chemistry In other words, the first ionization enthalpy for an element X is the enthalpy change ($\Delta_i H$) for the reaction depicted in equation 3.1. $X(g) \rightarrow X+(g) + e-$ (3.1) The ionization enthalpy is expressed in units of kJ mol–1. We can define the second ionization enthalpy as the energy required to remove the second most loosely bound electron; it is the energy required to carry out the reaction shown in equation 3.2. $X+(g) \rightarrow X2+(g) + e-$ (3.2) Energy is always required to remove electrons from an atom and hence ionization enthalpies are always positive. The second ionization enthalpy will be higher than the first ionization enthalpy because it is more difficult to remove an electron from a positively charged ion than from a neutral atom. In the same way the third ionization enthalpy will be higher than the second and so on. The term "ionization enthalpy", if not qualified, is taken as the first ionization enthalpy. The first ionization enthalpies of elements having atomic numbers up to 60 are plotted in Fig. 3.5. The periodicity of the graph is quite striking. You will find maxima at the noble gases which have closed electron shells and very stable electron configurations. On the other hand, minima occur at the alkali metals and their low ionization enthalpies Fig. 3.5 Variation of first ionization enthalpies ($\Delta_i H$) with atomic number for elements with Z = 1 to 60 can be correlated with their high reactivity. In addition, you will notice two trends the first ionization enthalpy generally increases as we go across a period and decreases as we descend in a group. These trends are illustrated in Figs. 3.6(a) and 3.6(b) respectively for the elements of the second period and the first group of the periodic table. You will appreciate that the ionization enthalpy and atomic radius are closely related properties. To understand these trends, we have to consider two factors : (i) the attraction of electrons towards the nucleus, and (ii) the repulsion of electrons from each other. The effective nuclear charge experienced by a Fig. 3.6(a) First ionization enthalpies ($\Delta_i H$) of elements of the second period as a function of atomic number (Z) and Fig. 3.6(b) $\Delta_i H$ of alkali metals as a function of Z. 3.6 (a) 3.6 (b) Rationalised 2023-24 Classification of Elements and Periodicity in Properties 89 valence electron in an atom will be less than the actual charge on the nucleus because of "shielding" or "screening" of the valence electron from the nucleus by the intervening core electrons. For example, the 2s electron in lithium is shielded from the nucleus by the inner core of 1s electrons. As a result, the valence electron experiences a net positive charge which is less than the actual charge of +3. In general, shielding is effective when the orbitals in the inner shells are completely filled. This situation occurs in the case of alkali metals which have single outermost ns-electron preceded by a noble gas electronic configuration. When we move from lithium to fluorine across the second period, successive electrons are added to orbitals in the same principal quantum level and the shielding of the nuclear charge by the inner core of electrons does not increase very much to compensate for the increased attraction of the electron to the nucleus. Thus, across a period, increasing nuclear charge outweighs the shielding. Consequently, the outermost electrons are held more and more tightly and the ionization enthalpy increases across a period. As we go down a group, the outermost electron being

increasingly farther from the nucleus, there is an increased shielding of the nuclear charge by the electrons in the inner levels. In this case, increase in shielding outweighs the increasing nuclear charge and the removal of the outermost electron requires less energy down a group. From Fig. 3.6(a), you will also notice that the first ionization enthalpy of boron (Z = 5) is slightly less than that of beryllium (Z = 4) even though the former has a greater nuclear charge. When we consider the same principal quantum level, an s-electron is attracted to the nucleus more than a p-electron. In beryllium, the electron removed during the ionization is an s-electron whereas the electron removed during ionization of boron is a p-electron. The penetration of a 2s-electron to the nucleus is more than that of a 2p-electron; hence the 2p electron of boron is more shielded from the nucleus by the inner core of electrons than the 2s electrons of beryllium. Therefore, it is easier to remove the 2p-electron from boron compared to the removal of a 2s- electron from beryllium. Thus, boron has a smaller first ionization enthalpy than beryllium. Another "anomaly" is the smaller first ionization enthalpy of oxygen compared to nitrogen. This arises because in the nitrogen atom, three 2p-electrons reside in different atomic orbitals (Hund's rule) whereas in the oxygen atom, two of the four 2p-electrons must occupy the same 2p-orbital resulting in an increased electron-electron repulsion. Consequently, it is easier to remove the fourth 2p-electron from oxygen than it is, to remove one of the three 2p-electrons from nitrogen. Problem 3.6 The first ionization enthalpy ($\Delta_i H$ ) values of the third period elements, Na, Mg and Si are respectively 496, 737 and 786 kJ mol$^{-1}$. Predict whether the first $\Delta_i H$ value for Al will be more close to 575 or 760 kJ mol$^{-1}$ ? Justify your answer. Solution It will be more close to 575 kJ mol$^{-1}$. The value for Al should be lower than that of Mg because of effective shielding of 3p electrons from the nucleus by 3s-electrons. (d) Electron Gain Enthalpy When an electron is added to a neutral gaseous atom (X) to convert it into a negative ion, the enthalpy change accompanying the process is defined as the Electron Gain Enthalpy ($\Delta_{eg}H$). Electron gain enthalpy provides a measure of the ease with which an atom adds an electron to form anion as represented by equation 3.3. $X(g) + e^- \rightarrow X^- (g)$ (3.3) Depending on the element, the process of adding an electron to the atom can be either endothermic or exothermic. For many elements energy is released when an electron is added to the atom and the electron gain enthalpy is negative. For example, group 17 elements (the halogens) have very high Rationalised 2023-24 90 chemistry negative electron gain enthalpies because they can attain stable noble gas electronic configurations by picking up an electron. On the other hand, noble gases have large positive electron gain enthalpies because the electron has to enter the next higher principal quantum level leading to a very unstable electronic configuration. It may be noted that electron gain enthalpies have large negative values toward the upper right of the periodic table preceding the noble gases. The variation in electron gain enthalpies of elements is less systematic than for ionization enthalpies. As a general rule, electron gain enthalpy becomes more negative with increase in the atomic number across a period. The effective nuclear charge increases from left to right across a period and consequently it will be easier to add an electron to a smaller atom since the added electron on an average would be closer to the positively charged nucleus. We should also expect electron gain enthalpy to become less negative as we go down a group because the size of the atom increases and the added electron would be farther from the nucleus. This is generally the case (Table 3.7). However, electron gain enthalpy of O or F is less negative than that of the succeeding element. This is because when an electron is added to O or F, the added electron goes to the smaller n = 2 quantum level and suffers significant repulsion from the other electrons present in this level. For the n = 3 quantum level (S or Cl), the added electron occupies a larger region of space and the electronelectron repulsion is much less. Problem 3.7 Which of the following will have the most negative electron gain enthalpy and which the least negative? P, S, Cl, F. Explain your answer. Solution Electron gain enthalpy generally becomes more negative across a period as we move from left to right. Within a group, electron gain enthalpy becomes less negative down a group. However, adding an electron to the 2p-orbital leads

to greater repulsion than adding an electron to the larger 3p-orbital. Hence the element with most negative electron gain enthalpy is chlorine; the one with the least negative electron gain enthalpy is phosphorus. (e) Electronegativity A qualitative measure of the ability of an atom in a chemical compound to attract shared electrons to itself is called electronegativity. Unlike ionization enthalpy and electron gain enthalpy, it is not a measureable quantity. However, a number of numerical scales of electronegativity of elements viz., Pauling scale, Mulliken-Jaffe scale, Allred-Rochow scale have been developed. The one which is the most widely used is the Pauling scale. Linus Pauling, an American scientist, in 1922 assigned arbitrarily a value of 4.0 to fluorine, the element considered to have the greatest * In many books, the negative of the enthalpy change for the process depicted in equation 3.3 is defined as the ELECTRON AFFINITY (A$_e$ ) of the atom under consideration. If energy is released when an electron is added to an atom, the electron affinity is taken as positive, contrary to thermodynamic convention. If energy has to be supplied to add an electron to an atom, then the electron affinity of the atom is assigned a negative sign. However, electron affinity is defined as absolute zero and, therefore at any other temperature (T) heat capacities of the reactants and the products have to be taken into account in $\Delta_{eg}H = -A_e - 5/2\ RT$. Table 3.7 Electron Gain Enthalpies* / (kJ mol$^{-1}$) of Some Main Group Elements

| Group 1 | $\Delta_{eg}H$ | Group 16 | $\Delta_{eg}H$ | Group 17 | $\Delta_{eg}H$ | Group 0 | $\Delta_{eg}H$ |
|---|---|---|---|---|---|---|---|
| H | – 73 | | | | | He | + 48 |
| Li | – 60 | O | – 141 | F | – 328 | Ne | + 116 |
| Na | – 53 | S | – 200 | Cl | – 349 | Ar | + 96 |
| K | – 48 | Se | – 195 | Br | – 325 | Kr | + 96 |
| Rb | – 47 | Te | – 190 | I | – 295 | Xe | + 77 |
| Cs | – 46 | Po | – 174 | At | – 270 | Rn | + 68 |

Rationalised 2023-24 Classification of Elements and Periodicity in Properties 91 ability to attract electrons. Approximate values for the electronegativity of a few elements are given in Table 3.8(a) The electronegativity of any given element is not constant; it varies depending on the element to which it is bound. Though it is not a measurable quantity, it does provide a means of predicting the nature of force that holds a pair of atoms together – a relationship that you will explore later. Electronegativity generally increases across a period from left to right (say from lithium to fluorine) and decreases down a group (say from fluorine to astatine) in the periodic table. How can these trends be explained? Can the electronegativity be related to atomic radii, which tend to decrease across each period from left to right, but increase down each group ? The attraction between the outer (or valence) electrons and the nucleus increases as the atomic radius decreases in a period. The electronegativity also increases. On the same account electronegativity values decrease with the increase in atomic radii down a group. The trend is similar to that of ionization enthalpy. Knowing the relationship between electronegativity and atomic radius, can you now visualise the relationship between electronegativity and non-metallic properties? Non-metallic elements have strong tendency Fig. 3.7 The periodic trends of elements in the periodic table Table 3.8(a) Electronegativity Values (on Pauling scale) Across the Periods

| Atom (Period II) | Li | Be | B | C | N | O | F |
|---|---|---|---|---|---|---|---|
| Electronegativity | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 | 3.5 | 4.0 |
| Atom (Period III) | Na | Mg | Al | Si | P | S | Cl |
| Electronegativity | 0.9 | 1.2 | 1.5 | 1.8 | 2.1 | 2.5 | 3.0 |

Table 3.8(b) Electronegativity Values (on Pauling scale) Down a Family

| Atom (Group I) | Electronegativity Value | Atom (Group 17) | Electronegativity Value |
|---|---|---|---|
| Li | 1.0 | F | 4.0 |
| Na | 0.9 | Cl | 3.0 |
| K | 0.8 | Br | 2.8 |
| Rb | 0.8 | I | 2.5 |
| Cs | 0.7 | At | 2.2 |

Rationalised 2023-24 92 chemistry to gain electrons. Therefore, electronegativity is directly related to that non-metallic properties of elements. It can be further extended to say that the electronegativity is inversely related to the metallic properties of elements. Thus, the increase in electronegativities across a period is accompanied by an increase in non-metallic properties (or decrease in metallic properties) of elements. Similarly, the decrease in electronegativity down a group is accompanied by a decrease in non-metallic properties (or increase in metallic properties) of elements. All these periodic trends are summarised in Figure 3.7. 3.7.2 Periodic Trends in Chemical Properties Most of the trends in chemical properties of elements, such as diagonal relationships, inert pair effect, effects of lanthanoid contraction etc. will be dealt with along the discussion of each group in later units. In this section we shall study the periodicity of the valence state shown by elements and the anomalous properties of the second period elements (from lithium to fluorine). (a) Periodicity of

Valence or Oxidation States The valence is the most characteristic property of the elements and can be understood in terms of their electronic configurations. The valence of representative elements is usually (though not necessarily) equal to the number of electrons in the outermost orbitals and/or equal to eight minus the number of outermost electrons as shown below. Nowadays the term oxidation state is frequently used for valence. Consider the two oxygen containing compounds: $OF_2$ and $Na_2O$. The order of electronegativity of the three elements involved in these compounds is F > O > Na. Each of the atoms of fluorine, with outer electronic configuration $2s^2 2p^5$, shares one electron with oxygen in the $OF_2$ molecule. Being highest electronegative element, fluorine is given oxidation state –1. Since there are two fluorine atoms in this molecule, oxygen with outer electronic configuration $2s^2 2p^4$ shares two electrons with fluorine atoms and thereby exhibits oxidation state +2. In $Na_2O$, oxygen being more electronegative accepts two electrons, one from each of the two sodium atoms and, thus, shows oxidation state –2. On the other hand sodium with electronic configuration $3s^1$ loses one electron to oxygen and is given oxidation state +1. Thus, the oxidation state of an element in a particular compound can be defined as the charge acquired by its atom on the basis of electronegative consideration from other atoms in the molecule. Problem 3.8 Using the Periodic Table, predict the formulas of compounds which might be formed by the following pairs of elements; (a) silicon and bromine (b) aluminium and sulphur. Solution (a) Silicon is group 14 element with a valence of 4; bromine belongs to the halogen family with a valence of 1. Hence the formula of the compound formed would be $SiBr_4$. (b) Aluminium belongs to group 13 with a valence of 3; sulphur belongs to group 16 elements with a valence of 2. Hence, the formula of the compound formed would be $Al_2S_3$. Some periodic trends observed in the valence of elements (hydrides and oxides) are shown in Table 3.9. Other such periodic trends which occur in the chemical behaviour of the elements are discussed elsewhere in

| Group | 1 | 2 | 13 | 14 | 15 | 16 | 17 | 18 |
|---|---|---|---|---|---|---|---|---|
| Number of valence electron | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| Valence | 1 | 2 | 3 | 4 | 3,5 | 2,6 | 1,7 | 0,8 |

Rationalised 2023-24 Classification of Elements and Periodicity in Properties 93 this book. There are many elements which exhibit variable valence. This is particularly characteristic of transition elements and actinoids, which we shall study later. (b) Anomalous Properties of Second Period Elements The first element of each of the groups 1 (lithium) and 2 (beryllium) and groups 13-17 (boron to fluorine) differs in many respects from the other members of their respective group. For example, lithium unlike other alkali metals, and beryllium unlike other alkaline earth metals, form compounds with pronounced covalent character; the other members of these groups predominantly form ionic compounds. In fact the behaviour of lithium and beryllium is more similar with

Table 3.9 Periodic Trends in Valence of Elements as shown by the Formulas of Their Compounds

| Group | 1 | 2 | 13 | 14 | 15 | 16 | 17 |
|---|---|---|---|---|---|---|---|
| Formula of hydride | LiH NaH KH | CaH2 | B2H6 AlH3 | CH4 SiH4 GeH4 SnH4 | NH3 PH3 AsH3 | H2O H2S H2Se H2Te | HF HCl HBr HI |
| Formula of oxide | Li2O Na2O K2O | MgO CaO SrO BaO | B2O3 Al2O3 Ga2O3 In2O3 | CO2 SiO2 GeO2 SnO2 PbO2 | N2O3, N2O5 P4O6, P4O10 As2O3, As2O5 Sb2O3, Sb2O5 Bi2O3 | – SO3 SeO3 TeO3 – | – Cl2O7 – – |

| Property | Element | | | | | |
|---|---|---|---|---|---|---|
| Metallic radius M/pm | Li 152 | Na 186 | Be 111 | Mg 160 | B 88 | Al 143 |
| Ionic radius M+/pm | Li 76 | Na 102 | Be 31 | Mg 72 | | |

the second element of the following group i.e., magnesium and aluminium, respectively. This sort of similarity is commonly referred to as diagonal relationship in the periodic properties. What are the reasons for the different chemical behaviour of the first member of a group of elements in the s- and p-blocks compared to that of the subsequent members in the same group? The anomalous behaviour is attributed to their small size, large charge/ radius ratio and high electronegativity of the elements. In addition, the first member of group has only four valence orbitals (2s and 2p) available for bonding, whereas the second member of the groups have nine valence orbitals (3s, 3p, 3d). As a consequence of this, the maximum covalency of the first member of each group is 4 (e.g., boron can only form - $BF_4^-$ , whereas the other members of the groups can expand their valence shell to accommodate more than four pairs of electrons e.g., aluminium $AlF_6^{3-}$ forms). Furthermore, the first member of p-block elements displays greater ability to form $p\pi$ –

pπ multiple bonds to itself (e.g., C = C, C ≡ C, N = N, N ≡ N) and to other second period elements (e.g., C = O, C = N, C ≡ N, N = O) compared to subsequent members of the same group. Rationalised 2023-24 94 chemistry Problem 3.9 Are the oxidation state and covalency of Al in [AlCl(H2O)5] 2+ same ? Solution No. The oxidation state of Al is +3 and the covalency is 6. 3.7.3 Periodic Trends and Chemical Reactivity We have observed the periodic trends in certain fundamental properties such as atomic and ionic radii, ionization enthalpy, electron gain enthalpy and valence. We know by now that the periodicity is related to electronic configuration. That is, all chemical and physical properties are a manifestation of the electronic configuration of elements. We shall now try to explore relationships between these fundamental properties of elements with their chemical reactivity. The atomic and ionic radii, as we know, generally decrease in a period from left to right. As a consequence, the ionization enthalpies generally increase (with some exceptions as outlined in section 3.7.1(a)) and electron gain enthalpies become more negative across a period. In other words, the ionization enthalpy of the extreme left element in a period is the least and the electron gain enthalpy of the element on the extreme right is the highest negative (note : noble gases having completely filled shells have rather positive electron gain enthalpy values). This results into high chemical reactivity at the two extremes and the lowest in the centre. Thus, the maximum chemical reactivity at the extreme left (among alkali metals) is exhibited by the loss of an electron leading to the formation of a cation and at the extreme right (among halogens) shown by the gain of an electron forming an anion. This property can be related with the reducing and oxidizing behaviour of the elements which you will learn later. However, here it can be directly related to the metallic and non-metallic character of elements. Thus, the metallic character of an element, which is highest at the extremely left decreases and the non-metallic character increases while moving from left to right across the period. The chemical reactivity of an element can be best shown by its reactions with oxygen and halogens. Here, we shall consider the reaction of the elements with oxygen only. Elements on two extremes of a period easily combine with oxygen to form oxides. The normal oxide formed by the element on extreme left is the most basic (e.g., Na2O), whereas that formed by the element on extreme right is the most acidic (e.g., Cl2O7). Oxides of elements in the centre are amphoteric (e.g., Al2O3, As2O3) or neutral (e.g., CO, NO, N2O). Amphoteric oxides behave as acidic with bases and as basic with acids, whereas neutral oxides have no acidic or basic properties. Problem 3.10 Show by a chemical reaction with water that Na2O is a basic oxide and Cl2O7 is an acidic oxide. Solution Na2O with water forms a strong base whereas Cl2O7 forms strong acid. Na2O + H2O → 2NaOH Cl2O7 + H2O → 2HClO4 Their basic or acidic nature can be qualitatively tested with litmus paper. Among transition metals (3d series), the change in atomic radii is much smaller as compared to those of representative elements across the period. The change in atomic radii is still smaller among inner-transition metals (4f series). The ionization enthalpies are intermediate between those of s- and p-blocks. As a consequence, they are less electropositive than group 1 and 2 metals. Rationalised 2023-24 Classification of Elements and Periodicity in Properties 95 In a group, the increase in atomic and ionic radii with increase in atomic number generally results in a gradual decrease in ionization enthalpies and a regular decrease (with exception in some third period elements as shown in section 3.7.1(d)) in electron gain enthalpies in the case of main group elements. Thus, the metallic character increases down the group and non-metallic character decreases. This trend can be related with their reducing and oxidizing property which you will learn later. In the case of transition elements, however, a reverse trend is observed. This can be explained in terms of atomic size and ionization enthalpy. SUMMARY In this Unit, you have studied the development of the Periodic Law and the Periodic Table. Mendeleev's Periodic Table was based on atomic masses. Modern Periodic Table arranges the elements in the order of their atomic numbers in seven horizontal rows (periods) and eighteen vertical columns (groups or families). Atomic numbers in a period are consecutive, whereas in a group they increase in a pattern. Elements of the same group have similar valence shell electronic

configuration and, therefore, exhibit similar chemical properties. However, the elements of the same period have incrementally increasing number of electrons from left to right, and, therefore, have different valencies. Four types of elements can be recognized in the periodic table on the basis of their electronic configurations. These are s-block, p-block, d-block and f-block elements. Hydrogen with one electron in the 1s orbital occupies a unique position in the periodic table. Metals comprise more than seventy eight per cent of the known elements. Non-metals, which are located at the top of the periodic table, are less than twenty in number. Elements which lie at the border line between metals and non-metals (e.g., Si, Ge, As) are called metalloids or semi-metals. Metallic character increases with increasing atomic number in a group whereas decreases from left to right in a period. The physical and chemical properties of elements vary periodically with their atomic numbers. Periodic trends are observed in atomic sizes, ionization enthalpies, electron gain enthalpies, electronegativity and valence. The atomic radii decrease while going from left to right in a period and increase with atomic number in a group. Ionization enthalpies generally increase across a period and decrease down a group. Electronegativity also shows a similar trend. Electron gain enthalpies, in general, become more negative across a period and less negative down a group. There is some periodicity in valence, for example, among representative elements, the valence is either equal to the number of electrons in the outermost orbitals or eight minus this number. Chemical reactivity is highest at the two extremes of a period and is lowest in the centre. The reactivity on the left extreme of a period is because of the ease of electron loss (or low ionization enthalpy). Highly reactive elements do not occur in nature in free state; they usually occur in the combined form. Oxides formed of the elements on the left are basic and of the elements on the right are acidic in nature. Oxides of elements in the centre are amphoteric or neutral. Rationalised 2023-24 96 chemistry Exercises 3.1 What is the basic theme of organisation in the periodic table? 3.2 Which important property did Mendeleev use to classify the elements in his periodic table and did he stick to that? 3.3 What is the basic difference in approach between the Mendeleev's Periodic Law and the Modern Periodic Law? 3.4 On the basis of quantum numbers, justify that the sixth period of the periodic table should have 32 elements. 3.5 In terms of period and group where would you locate the element with Z =114? 3.6 Write the atomic number of the element present in the third period and seventeenth group of the periodic table. 3.7 Which element do you think would have been named by (i) Lawrence Berkeley Laboratory (ii) Seaborg's group? 3.8 Why do elements in the same group have similar physical and chemical properties? 3.9 What does atomic radius and ionic radius really mean to you? 3.10 How do atomic radius vary in a period and in a group? How do you explain the variation? 3.11 What do you understand by isoelectronic species? Name a species that will be isoelectronic with each of the following atoms or ions. (i) F– (ii) Ar (iii) $Mg^{2+}$ (iv) $Rb^+$ 3.12 Consider the following species : $N^{3-}$, $O^{2-}$, F– , $Na^+$, $Mg^{2+}$ and $Al^{3+}$ (a) What is common in them? (b) Arrange them in the order of increasing ionic radii. 3.13 Explain why cation are smaller and anions larger in radii than their parent atoms? 3.14 What is the significance of the terms — 'isolated gaseous atom' and 'ground state' while defining the ionization enthalpy and electron gain enthalpy? Hint : Requirements for comparison purposes. 3.15 Energy of an electron in the ground state of the hydrogen atom is –2.18×$10^{-18}$J. Calculate the ionization enthalpy of atomic hydrogen in terms of J $mol^{-1}$. Hint: Apply the idea of mole concept to derive the answer. 3.16 Among the second period elements the actual ionization enthalpies are in the order Li < B < Be < C < O < N < F < Ne. Explain why (i) Be has higher $\Delta_i$H than B (ii) O has lower $\Delta_i$H than N and F? Rationalised 2023-24 Classification of Elements and Periodicity in Properties 97 3.17 How would you explain the fact that the first ionization enthalpy of sodium is lower than that of magnesium but its second ionization enthalpy is higher than that of magnesium? 3.18 What are the various factors due to which the ionization enthalpy of the main group elements tends to decrease down a group? 3.19 The first ionization enthalpy values (in kJ $mol^{-1}$) of group 13 elements are : B Al Ga In Tl 801 577 579 558 589 How would you explain this deviation

from the general trend ? 3.20 Which of the following pairs of elements would have a more negative electron gain enthalpy? (i) O or F (ii) F or Cl 3.21 Would you expect the second electron gain enthalpy of O as positive, more negative or less negative than the first? Justify your answer. 3.22 What is the basic difference between the terms electron gain enthalpy and electronegativity? 3.23 How would you react to the statement that the electronegativity of N on Pauling scale is 3.0 in all the nitrogen compounds? 3.24 Describe the theory associated with the radius of an atom as it (a) gains an electron (b) loses an electron 3.25 Would you expect the first ionization enthalpies for two isotopes of the same element to be the same or different? Justify your answer. 3.26 What are the major differences between metals and non-metals? 3.27 Use the periodic table to answer the following questions. (a) Identify an element with five electrons in the outer subshell. (b) Identify an element that would tend to lose two electrons. (c) Identify an element that would tend to gain two electrons. (d) Identify the group having metal, non-metal, liquid as well as gas at the room temperature. 3.28 The increasing order of reactivity among group 1 elements is Li < Na < K < Rb Cl > Br > I. Explain. 3.29 Write the general outer electronic configuration of s-, p-, d- and f- block elements. 3.30 Assign the position of the element having outer electronic configuration (i) ns2np4 for n=3 (ii) (n-1)d2ns2 for n=4, and (iii) (n-2) f 7 (n-1)d1ns2 for n=6, in the periodic table. Rationalised 2023-24 98 chemistry 3.31 The first ($\Delta i$ H1) and the second ($\Delta i$ H2) ionization enthalpies (in kJ mol−1) and the ($\Delta egH$) electron gain enthalpy (in kJ mol−1) of a few elements are given below: Elements $\Delta H1$ $\Delta H2$ $\Delta egH$ I 520 7300 −60 II 419 3051 −48 III 1681 3374 −328 IV 1008 1846 −295 V 2372 5251 +48 VI 738 1451 −40 Which of the above elements is likely to be : (a) the least reactive element. (b) the most reactive metal. (c) the most reactive non-metal. (d) the least reactive non-metal. (e) the metal which can form a stable binary halide of the formula MX2(X=halogen). (f) the metal which can form a predominantly stable covalent halide of the formula MX (X=halogen)? 3.32 Predict the formulas of the stable binary compounds that would be formed by the combination of the following pairs of elements. (a) Lithium and oxygen (b) Magnesium and nitrogen (c) Aluminium and iodine (d) Silicon and oxygen (e) Phosphorus and fluorine (f) Element 71 and fluorine 3.33 In the modern periodic table, the period indicates the value of : (a) atomic number (b) atomic mass (c) principal quantum number (d) azimuthal quantum number. 3.34 Which of the following statements related to the modern periodic table is incorrect? (a) The p-block has 6 columns, because a maximum of 6 electrons can occupy all the orbitals in a p-shell. (b) The d-block has 8 columns, because a maximum of 8 electrons can occupy all the orbitals in a d-subshell. (c) Each block contains a number of columns equal to the number of electrons that can occupy that subshell. (d) The block indicates value of azimuthal quantum number (l) for the last subshell that received electrons in building up the electronic configuration. Rationalised 2023-24 Classification of Elements and Periodicity in Properties 99 3.35 Anything that influences the valence electrons will affect the chemistry of the element. Which one of the following factors does not affect the valence shell? (a) Valence principal quantum number (n) (b) Nuclear charge (Z ) (c) Nuclear mass (d) Number of core electrons. 3.36 The size of isoelectronic species — F− , Ne and Na+ is affected by (a) nuclear charge (Z ) (b) valence principal quantum number (n) (c) electron-electron interaction in the outer orbitals (d) none of the factors because their size is the same. 3.37 Which one of the following statements is incorrect in relation to ionization enthalpy? (a) Ionization enthalpy increases for each successive electron. (b) The greatest increase in ionization enthalpy is experienced on removal of electron from core noble gas configuration. (c) End of valence electrons is marked by a big jump in ionization enthalpy. (d) Removal of electron from orbitals bearing lower n value is easier than from orbital having higher n value. 3.38 Considering the elements B, Al, Mg, and K, the correct order of their metallic character is : (a) B > Al > Mg > K (b) Al > Mg > B > K (c) Mg > Al > K > B (d) K > Mg > Al > B 3.39 Considering the elements B, C, N, F, and Si, the correct order of their non-metallic character is : (a) B > C > Si > N > F (b) Si > C > B > N > F (c) F > N > C > B > Si (d) F > N > C > Si > B 3.40 Considering the elements F, Cl, O and N, the correct order of their

chemical reactivity in terms of oxidizing property is : (a) F > Cl > O > N (b) F > O > Cl > N (c) Cl > F > O > N (d) O > F > N > Cl Rationalised 2023-24Scientists are constantly discovering new compounds, orderly arranging the facts about them, trying to explain with the existing knowledge, organising to modify the earlier views or evolve theories for explaining the newly observed facts. Unit 4 After studying this Unit, you will be able to • u n d e r s t a n d Kössel-Lewis approach to chemical bonding; • explain the octet rule and its limitations, draw Lewis structures of simple molecules; • explain the formation of different types of bonds; • describe the VSEPR theory and predict the geometry of simple molecules; • explain the valence bond approach for the formation of covalent bonds; • predict the directional properties of covalent bonds; • explain the different types of hybridisation involving s, p and d orbitals and draw shapes of simple covalent molecules; • describe the molecular orbital theory of homonuclear diatomic molecules; • explain the concept of hydrogen bond. CHEMICAL BONDING AND MOLECULAR STRUCTURE Matter is made up of one or different type of elements. Under normal conditions no other element exists as an independent atom in nature, except noble gases. However, a group of atoms is found to exist together as one species having characteristic properties. Such a group of atoms is called a molecule. Obviously there must be some force which holds these constituent atoms together in the molecules. The attractive force which holds various constituents (atoms, ions, etc.) together in different chemical species is called a chemical bond. Since the formation of chemical compounds takes place as a result of combination of atoms of various elements in different ways, it raises many questions. Why do atoms combine? Why are only certain combinations possible? Why do some atoms combine while certain others do not? Why do molecules possess definite shapes? To answer such questions different theories and concepts have been put forward from time to time. These are Kössel-Lewis approach, Valence Shell Electron Pair Repulsion (VSEPR) Theory, Valence Bond (VB) Theory and Molecular Orbital (MO) Theory. The evolution of various theories of valence and the interpretation of the nature of chemical bonds have closely been related to the developments in the understanding of the structure of atom, the electronic configuration of elements and the periodic table. Every system tends to be more stable and bonding is nature's way of lowering the energy of the system to attain stability. Rationalised 2023-24 Chemical Bonding And Molecular Structure 101 4.1 KÖssel-Lew is Approach to Chemical Bonding In order to explain the formation of chemical bond in terms of electrons, a number of attempts were made, but it was only in 1916 when Kössel and Lewis succeeded independently in giving a satisfactory explanation. They were the first to provide some logical explanation of valence which was based on the inertness of noble gases. Lewis pictured the atom in terms of a positively charged 'Kernel' (the nucleus plus the inner electrons) and the outer shell that could accommodate a maximum of eight electrons. He, further assumed that these eight electrons occupy the corners of a cube which surround the 'Kernel'. Thus the single outer shell electron of sodium would occupy one corner of the cube, while in the case of a noble gas all the eight corners would be occupied. This octet of electrons, represents a particularly stable electronic arrangement. Lewis postulated that atoms achieve the stable octet when they are linked by chemical bonds. In the case of sodium and chlorine, this can happen by the transfer of an electron from sodium to chlorine thereby giving the Na+ and Cl– ions. In the case of other molecules like Cl2, H2, F2, etc., the bond is formed by the sharing of a pair of electrons between the atoms. In the process each atom attains a stable outer octet of electrons. Lewis Symbols: In the formation of a molecule, only the outer shell electrons take part in chemical combination and they are known as valence electrons. The inner shell electrons are well protected and are generally not involved in the combination process. G.N. Lewis, an American chemist introduced simple notations to represent valence electrons in an atom. These notations are called Lewis symbols. For example, the Lewis symbols for the elements of second period are as under: Significance of Lewis Symbols : The number of dots around the symbol represents the number of valence electrons. This number of valence electrons helps to calculate the common or group

valence of the element. The group valence of the elements is generally either equal to the number of dots in Lewis symbols or 8 minus the number of dots or valence electrons. Kössel, in relation to chemical bonding, drew attention to the following facts: • In the periodic table, the highly electronegative halogens and the highly electropositive alkali metals are separated by the noble gases; • The formation of a negative ion from a halogen atom and a positive ion from an alkali metal atom is associated with the gain and loss of an electron by the respective atoms; • The negative and positive ions thus formed attain stable noble gas electronic configurations. The noble gases (with the exception of helium which has a duplet of electrons) have a particularly stable outer shell configuration of eight (octet) electrons, $ns^2np^6$. • The negative and positive ions are stabilized by electrostatic attraction. For example, the formation of NaCl from sodium and chlorine, according to the above scheme, can be explained as: Na $\rightarrow$ Na+ + e– [Ne] 3s1 [Ne] Cl + e– $\rightarrow$ Cl– [Ne] 3s2 3p5 [Ne] 3s2 3p6 or [Ar] Na+ + Cl– $\rightarrow$ NaCl or Na+Cl– Similarly the formation of CaF2 may be shown as: Ca $\rightarrow$ Ca2+ + 2e– [Ar]4s2 [Ar] F + e– $\rightarrow$ F– [He] 2s2 2p5 [He] 2s2 2p6 or [Ne] Ca2+ + 2F– $\rightarrow$ CaF2 or Ca2+(F–)2 The bond formed, as a result of the electrostatic attraction between the positive and negative ions was termed as 102 chemistry the electrovalent bond. The electrovalence is thus equal to the number of unit charge(s) on the ion. Thus, calcium is assigned a positive electrovalence of two, while chlorine a negative electrovalence of one. Kössel's postulations provide the basis for the modern concepts regarding ion-formation by electron transfer and the formation of ionic crystalline compounds. His views have proved to be of great value in the understanding and systematisation of the ionic compounds. At the same time he did recognise the fact that a large number of compounds did not fit into these concepts. 4.1.1 Octet Rule Kössel and Lewis in 1916 developed an important theory of chemical combination between atoms known as electronic theory of chemical bonding. According to this, atoms can combine either by transfer of valence electrons from one atom to another (gaining or losing) or by sharing of valence electrons in order to have an octet in their valence shells. This is known as octet rule. 4.1.2 Covalent Bond Langmuir (1919) refined the Lewis postulations by abandoning the idea of the stationary cubical arrangement of the octet, and by introducing the term covalent bond. The Lewis-Langmuir theory can be understood by considering the formation of the chlorine molecule, Cl2. The Cl atom with electronic configuration, [Ne]3s2 3p5, is one electron short of the argon configuration. The formation of the Cl2 molecule can be understood in terms of the sharing of a pair of electrons between the two chlorine atoms, each chlorine atom contributing one electron to the shared pair. In the process both chlorine atoms attain the outer shell octet of the nearest noble gas (i.e., argon). The dots represent electrons. Such structures are referred to as Lewis dot structures. The Lewis dot structures can be written for other molecules also, in which the combining atoms may be identical or different. The important conditions being that: • Each bond is formed as a result of sharing of an electron pair between the atoms. • Each combining atom contributes at least one electron to the shared pair. • The combining atoms attain the outershell noble gas configurations as a result of the sharing of electrons. • Thus in water and carbon tetrachloride molecules, formation of covalent bonds can be represented as: or Cl – Cl Covalent bond between two Cl atoms Thus, when two atoms share one electron pair they are said to be joined by a single covalent bond. In many compounds we have multiple bonds between atoms. The formation of multiple bonds envisages sharing of more than one electron pair between two atoms. If two atoms share two pairs of electrons, the covalent bond between them is called a double bond. For example, in the carbon dioxide molecule, we have two double bonds between the carbon and oxygen atoms. Similarly in ethene molecule the two carbon atoms are joined by a double bond. Double bonds in CO2 molecule Chemical Bonding And Molecular Structure 103 When combining atoms share three electron pairs as in the case of two nitrogen atoms in the N2 molecule and the two carbon atoms in the ethyne molecule, a triple bond is formed. N2 molecule C2H2 molecule 4.1.3 Lewis Representation of Simple Molecules (the Lewis Structures) The

Lewis dot structures provide a picture of bonding in molecules and ions in terms of the shared pairs of electrons and the octet rule. While such a picture may not explain the bonding and behaviour of a molecule completely, it does help in understanding the formation and properties of a molecule to a large extent. Writing of Lewis dot structures of molecules is, therefore, very useful. The Lewis dot structures can be written by adopting the following steps: • The total number of electrons required for writing the structures are obtained by adding the valence electrons of the combining atoms. For example, in the $CH_4$ molecule there are eight valence electrons available for bonding (4 from carbon and 4 from the four hydrogen atoms). • For anions, each negative charge would mean addition of one electron. For cations, each positive charge would result in subtraction of one electron from the total number of valence electrons. For example, for the $CO_3^{2-}$ ion, the two negative charges indicate that there are two additional electrons than those provided by the neutral atoms. For $NH_4^+$ ion, one positive charge indicates the loss of one electron from the group of neutral atoms. • Knowing the chemical symbols of the combining atoms and having knowledge of the skeletal structure of the compound (known or guessed intelligently), it is easy to distribute the total number of electrons as bonding shared pairs between the atoms in proportion to the total bonds. • In general the least electronegative atom occupies the central position in the molecule/ion. For example in the $NF_3$ and $CO_3^{2-}$, nitrogen and carbon are the central atoms whereas fluorine and oxygen occupy the terminal positions. • After accounting for the shared pairs of electrons for single bonds, the remaining electron pairs are either utilized for multiple bonding or remain as the lone pairs. The basic requirement being that each bonded atom gets an octet of electrons. Lewis representations of a few molecules/ ions are given in Table 4.1. Table 4.1 The Lewis Representation of Some Molecules * Each H atom attains the configuration of helium (a duplet of electrons) $C_2H_4$ molecule Rationalised 2023-24 104 chemistry Problem 4.1 Write the Lewis dot structure of CO molecule. Solution Step 1. Count the total number of valence electrons of carbon and oxygen atoms. The outer (valence) shell configurations of carbon and oxygen atoms are: $2s^2 2p^2$ and $2s^2 2p^4$, respectively. The valence electrons available are 4 + 6 =10. Step 2. The skeletal structure of CO is written as: C O Step 3. Draw a single bond (one shared electron pair) between C and O and complete the octet on O, the remaining two electrons are the lone pair on C. This does not complete the octet on carbon and hence we have to resort to multiple bonding (in this case a triple bond) between C and O atoms. This satisfies the octet rule condition for both atoms. Problem 4.2 Write the Lewis structure of the nitrite ion, $NO_2^-$ . Solution Step 1. Count the total number of valence electrons of the nitrogen atom, the oxygen atoms and the additional one negative charge (equal to one electron). $N(2s^2 2p^3)$, O $(2s^2 2p^4)$ 5 + (2 × 6) +1 = 18 electrons Step 2. The skeletal structure of $NO_2^-$ is written as : O N O Step 3. Draw a single bond (one shared electron pair) between the nitrogen and each of the oxygen atoms completing the octets on oxygen atoms. This, however, does not complete the octet on nitrogen if the remaining two electrons constitute lone pair on it. Hence we have to resort to multiple bonding between nitrogen and one of the oxygen atoms (in this case a double bond). This leads to the following Lewis dot structures. 4.1.4 Formal Charge Lewis dot structures, in general, do not represent the actual shapes of the molecules. In case of polyatomic ions, the net charge is possessed by the ion as a whole and not by a particular atom. It is, however, feasible to assign a formal charge on each atom. The formal charge of an atom in a polyatomic molecule or ion may be defined as the difference between the number of valence electrons of that atom in an isolated or free state and the number of electrons assigned to that atom in the Lewis structure. It is expressed as : Formal charge (F.C.) on an atom in a Lewis structure = total number of valence electrons in the free atom — total number of non bonding (lone pair) electrons — (1/2) total number of bonding (shared) electrons Rationalised 2023-24 Chemical Bonding And Molecular Structure 105 4.1.5 Limitations of the Octet Rule The octet rule, though useful, is not universal. It is quite useful for understanding the structures of most of the organic compounds and it applies mainly to the second period elements of

the periodic table. There are three types of exceptions to the octet rule. The incomplete octet of the central atom In some compounds, the number of electrons surrounding the central atom is less than eight. This is especially the case with elements having less than four valence electrons. Examples are $LiCl$, $BeH_2$ and $BCl_3$. Li, Be and B have 1, 2 and 3 valence electrons only. Some other such compounds are $AlCl_3$ and $BF_3$. Odd-electron molecules In molecules with an odd number of electrons like nitric oxide, NO and nitrogen dioxide, $NO_2$, the octet rule is not satisfied for all the atoms The expanded octet Elements in and beyond the third period of the periodic table have, apart from 3s and 3p orbitals, 3d orbitals also available for bonding. In a number of compounds of these elements there are more than eight valence electrons around the central atom. This is termed as the expanded octet. Obviously the octet rule does not apply in such cases. Some of the examples of such compounds are: $PF_5$, $SF_6$, $H_2SO_4$ and a number of coordination compounds. The counting is based on the assumption that the atom in the molecule owns one electron of each shared pair and both the electrons of a lone pair. Let us consider the ozone molecule ($O_3$). The Lewis structure of $O_3$ may be drawn as: The atoms have been numbered as 1, 2 and 3. The formal charge on: • The central O atom marked 1 = 6 − 2 − 1 2 (6) = +1 • The end O atom marked 2 = 6 − 4 − 1 2 (4) = 0 • The end O atom marked 3 = 6 − 6 − 1 2 (2) = −1 Hence, we represent $O_3$ along with the formal charges as follows: We must understand that formal charges do not indicate real charge separation within the molecule. Indicating the charges on the atoms in the Lewis structure only helps in keeping track of the valence electrons in the molecule. Formal charges help in the selection of the lowest energy structure from a number of possible Lewis structures for a given species. Generally the lowest energy structure is the one with the smallest formal charges on the atoms. The formal charge is a factor based on a pure covalent view of bonding in which electron pairs are shared equally by neighbouring atoms. Rationalised 2023-24 106 chemistry Interestingly, sulphur also forms many compounds in which the octet rule is obeyed. In sulphur dichloride, the S atom has an octet of electrons around it. Other drawbacks of the octet theory • It is clear that octet rule is based upon the chemical inertness of noble gases. However, some noble gases (for example xenon and krypton) also combine with oxygen and fluorine to form a number of compounds like $XeF_2$, $KrF_2$, $XeOF_2$ etc. • This theory does not account for the shape of molecules. • It does not explain the relative stability of the molecules being totally silent about the energy of a molecule. 4.2 Ionic or Electrovalent Bond From the Kössel and Lewis treatment of the formation of an ionic bond, it follows that the formation of ionic compounds would primarily depend upon: • The ease of formation of the positive and negative ions from the respective neutral atoms; • The arrangement of the positive and negative ions in the solid, that is, the lattice of the crystalline compound. The formation of a positive ion involves ionization, i.e., removal of electron(s) from the neutral atom and that of the negative ion involves the addition of electron(s) to the neutral atom. $M(g) \rightarrow M^+(g) + e^-$ ; Ionization enthalpy $X(g) + e^- \rightarrow X^-(g)$ ; Electron gain enthalpy $M^+(g) + X^-(g) \rightarrow MX(s)$ The electron gain enthalpy, $\Delta_{eg}H$, is the enthalpy change (Unit 3), when a gas phase atom in its ground state gains an electron. The electron gain process may be exothermic or endothermic. The ionization, on the other hand, is always endothermic. Electron affinity, is the negative of the energy change accompanying electron gain. Obviously ionic bonds will be formed more easily between elements with comparatively low ionization enthalpies and elements with comparatively high negative value of electron gain enthalpy. Most ionic compounds have cations derived from metallic elements and anions from non-metallic elements. The ammonium ion, $NH_4^+$ (made up of two non-metallic elements) is an exception. It forms the cation of a number of ionic compounds. Ionic compounds in the crystalline state consist of orderly three-dimensional arrangements of cations and anions held together by coulombic interaction energies. These compounds crystallise in different crystal structures determined by the size of the ions, their packing arrangements and other factors. The crystal structure of sodium chloride, NaCl (rock salt), for example is shown below. Rock salt structure In ionic solids, the sum of

the electron gain enthalpy and the ionization enthalpy may be positive but still the crystal structure gets stabilized due to the energy released in the formation of the crystal lattice. For example: the ionization enthalpy for Na+(g) formation from Na(g) is 495.8 kJ mol–1 ; while the electron gain enthalpy for the change Cl(g) + e– → Cl– (g) is, – 348.7 kJ mol–1 only. The sum of the two, 147.1 kJ mol-1 is more than compensated for by the enthalpy of lattice formation of NaCl(s) (–788 kJ mol–1). Therefore, the energy released in the processes is more than the Rationalised 2023-24 Chemical Bonding And Molecular Structure 107 energy absorbed. Thus a qualitative measure of the stability of an ionic compound is provided by its enthalpy of lattice formation and not simply by achieving octet of electrons around the ionic species in gaseous state. Since lattice enthalpy plays a key role in the formation of ionic compounds, it is important that we learn more about it. 4.2.1 Lattice Enthalpy The Lattice Enthalpy of an ionic solid is defined as the energy required to completely separate one mole of a solid ionic compound into gaseous constituent ions. For example, the lattice enthalpy of NaCl is 788 kJ mol–1. This means that 788 kJ of energy is required to separate one mole of solid NaCl into one mole of Na+ (g) and one mole of Cl– (g) to an infinite distance. This process involves both the attractive forces between ions of opposite charges and the repulsive forces between ions of like charge. The solid crystal being threedimensional; it is not possible to calculate lattice enthalpy directly from the interaction of forces of attraction and repulsion only. Factors associated with the crystal geometry have to be included. 4.3 Bond Parameters 4.3.1 Bond Length Bond length is defined as the equilibrium distance between the nuclei of two bonded atoms in a molecule. Bond lengths are measured by spectroscopic, X-ray diffraction and electron-diffraction techniques about which you will learn in higher classes. Each atom of the bonded pair contributes to the bond length (Fig. 4.1). In the case of a covalent bond, the contribution from each atom is called the covalent radius of that atom. The covalent radius is measured approximately as the radius of an atom's core which is in contact with the core of an adjacent atom in a bonded situation. The covalent radius is half of the distance between two similar atoms joined by a covalent bond in the same molecule. The van der Waals radius represents the overall size of the atom which includes its valence shell in a nonbonded situation. Further, the van der Waals radius is half of the distance between two similar atoms in separate molecules in a solid. Covalent and van der Waals radii of chlorine are depicted in Fig. 4.2. Fig. 4.2 Covalent and van der Waals radii in a chlorine molecule. The inner circles correspond to the size of the chlorine atom (rvdw and rc are van der Waals and covalent radii respectively). r =c 99 pm 198 pm r = 180 pm vdw 360 pm Fig. 4.1 The bond length in a covalent molecule AB. R = rA + rB (R is the bond length and rA and rB are the covalent radii of atoms A and B respectively) Rationalised 2023-24 108 chemistry Some typical average bond lengths for single, double and triple bonds are shown in Table 4.2. Bond lengths for some common molecules are given in Table 4.3. The covalent radii of some common elements are listed in Table 4.4. 4.3.2 Bond Angle It is defined as the angle between the orbitals containing bonding electron pairs around the central atom in a molecule/complex ion. Bond angle is expressed in degree which can be experimentally determined by spectroscopic methods. It gives some idea regarding the distribution of orbitals around the central atom in a molecule/complex ion and hence it helps us in determining its shape. For example H–O–H bond angle in water can be represented as under : 4.3.3 Bond Enthalpy It is defined as the amount of energy required to break one mole of bonds of a particular type between two atoms in a gaseous state. The unit of bond enthalpy is kJ mol–1. For example, the H – H bond enthalpy in hydrogen molecule is 435.8 kJ mol–1. H2(g) → H(g) + H(g); $\Delta_a H_\varsigma$ = 435.8 kJ mol–1 Similarly the bond enthalpy for molecules containing multiple bonds, for example O2 and N2 will be as under : O2 (O = O) (g) → O(g) + O(g); $\Delta_a H_\varsigma$ = 498 kJ mol–1 N2 (N ≡ N) (g) → N(g) + N(g); $\Delta_a H_\varsigma$ = 946.0 kJ mol–1 It is important that larger the bond dissociation enthalpy, stronger will be the bond in the molecule. For a heteronuclear diatomic molecules like HCl, we have HCl (g) → H(g) + Cl (g); $\Delta_a H_\varsigma$ = 431.0 kJ mol–1 In case of polyatomic molecules, the measurement of bond strength is more complicated. For example

in case of $H_2O$ molecule, the enthalpy needed to break the two $O – H$ bonds is not the same. Table 4.2 Average Bond Lengths for Some Single, Double and Triple Bonds Bond Type Covalent Bond Length (pm) O–H C–H N–O C–O C–N C–C C=O N=O C=C C=N C≡N C≡C 96 107 136 143 143 154 121 122 133 138 116 120 Table 4.3 Bond Lengths in Some Common Molecules Molecule Bond Length (pm) $H_2$ (H – H) $F_2$ (F – F) $Cl_2$ (Cl – Cl) $Br_2$ (Br – Br) $I_2$ (I – I) $N_2$ (N ≡ N) $O_2$ (O = O) HF (H – F) HCl (H – Cl) HBr (H – Br) HI (H – I) 74 144 199 228 267 109 121 92 127 141 160 Table 4.4 Covalent Radii, *rcov/(pm) * The values cited are for single bonds, except where otherwise indicated in parenthesis. (See also Unit 3 for periodic trends). Rationalised 2023-24 Chemical Bonding And Molecular Structure 109 $H_2O(g) \rightarrow$ $H(g) + OH(g)$; $\Delta aH1$ ς = 502 kJ mol–1 OH(g) → H(g) + O(g); $\Delta aH2$ ς = 427 kJ mol–1 The difference in the $\Delta aH$ς value shows that the second $O – H$ bond undergoes some change because of changed chemical environment. This is the reason for some difference in energy of the same $O – H$ bond in different molecules like $C_2H_5OH$ (ethanol) and water. Therefore in polyatomic molecules the term mean or average bond enthalpy is used. It is obtained by dividing total bond dissociation enthalpy by the number of bonds broken as explained below in case of water molecule, Average bond enthalpy = 502 427 2 + = 464.5 kJ mol–1 4.3.4 Bond Order In the Lewis description of covalent bond, the Bond Order is given by the number of bonds between the two atoms in a molecule. The bond order, for example in $H_2$ (with a single shared electron pair), in $O_2$ (with two shared electron pairs) and in $N_2$ (with three shared electron pairs) is 1,2,3 respectively. Similarly in CO (three shared electron pairs between C and O) the bond order is 3. For $N_2$, bond order is 3 and its is 946 kJ mol–1; being one of the highest for a diatomic molecule. Isoelectronic molecules and ions have identical bond orders; for example, $F_2$ and $O_2$ 2– have bond order 1. $N_2$, CO and NO+ have bond order 3. A genera l corre lat ion use fu l for understanding the stablities of molecules is that: with increase in bond order, bond enthalpy increases and bond length decreases. 4.3.5 Resonance Structures Itis often observed that a single Lewis structure is inadequate for the representation of a molecule in conformity with its experimentally determined parameters. For example, the ozone, $O_3$ molecule can be equally represented by the structures I and II shown below: In both structures we have a O–O single bond and a O=O double bond. The normal O–O and O=O bond lengths are 148 pm and 121 pm respectively. Experimentally determined oxygen-oxygen bond lengths in the $O_3$ molecule are same (128 pm). Thus the oxygen-oxygen bonds in the $O_3$ molecule are intermediate between a double and a single bond. Obviously, this cannot be represented by either of the two Lewis structures shown above. The concept of resonance was introduced to deal with the type of difficulty experienced in the depiction of accurate structures of molecules like $O_3$. According to the concept of resonance, whenever a single Lewis structure cannot describe a molecule accurately, a number of structures with similar energy, positions of nuclei, bonding and non-bonding pairs of electrons are taken as the canonical structures of the hybrid which describes the molecule accurately. Thus for $O_3$, the two structures shown above constitute the canonical structures or resonance structures and their hybrid i.e., the III structure represents the structure of $O_3$ more accurately. This is also called resonance hybrid. Resonance is represented by a double headed arrow. Fig. 4.3 Resonance in the $O_3$ molecule (structures I and II represent the two canonical forms while the structure III is the resonance hybrid) Rationalised 2023-24 110 chemistry Some of the other examples of resonance structures are provided by the carbonate ion and the carbon dioxide molecule. Problem 4.3 Explain the structure of $CO_3$ 2– ion in terms of resonance. Solution The single Lewis structure based on the presence of two single bonds and one double bond between carbon and oxygen atoms is inadequate to represent the molecule accurately as it represents unequal bonds. According to the experimental findings, all carbon to oxygen bonds in $CO_3$ 2– are equivalent. Therefore the carbonate ion is best described as a resonance hybrid of the canonical forms I, II, and III shown below. Problem 4.4 Explain the structure of $CO_2$ molecule. Solution The experimentally determined carbon to oxygen bond length in $CO_2$ is 115 pm. The lengths of a normal carbon to oxygen double bond (C=O) and carbon to oxygen triple

bond (C≡O) are 121 pm and 110 pm respectively. The carbon-oxygen bond lengths in $CO_2$ (115 pm) lie between the values for C=O and C≡O. Obviously, a single Lewis structure cannot depict this position and it becomes necessary to write more than one Lewis structures and to consider that the structure of $CO_2$ is best described as a hybrid of the canonical or resonance forms I, II and III. In general, it may be stated that • Resonance stabilizes the molecule as the energy of the resonance hybrid is less than the energy of any single cannonical structure; and, • Resonance averages the bond characteristics as a whole. Thus the energy of the $O_3$ resonance hybrid is lower than either of the two cannonical froms I and II (Fig. 4.3). Many misconceptions are associated with resonance and the same need to be dispelled. You should remember that : • The cannonical forms have no real existence. • The molecule does not existfor a certain fraction of time in one cannonical form and for other fractions of time in other cannonical forms. • There is no such equilibrium between the cannonical forms as we have between tautomeric forms (keto and enol) in tautomerism. • The molecule as such has a single structure which is the resonance hybrid of the cannonical forms and which cannot as such be depicted by a single Lewis structure. 4.3.6 Polarity of Bonds The existence of a hundred percent ionic or covalent bond represents an ideal situation. In reality no bond or a compound is either completely covalent or ionic. Even in case of covalent bond between two hydrogen atoms, there is some ionic character. When covalent bond is formed between two similar atoms, for example in $H_2$, $O_2$, $Cl_2$, $N_2$ or $F_2$, the shared pair of electrons is equally attracted by the two atoms. As a result Fig. 4.4 Resonance in $CO_3^{2-}$, I, II and III represent the three canonical forms. Fig. 4.5 Resonance in $CO_2$ molecule, I, II and III represent the three canonical forms. Rationalised 2023-24 Chemical Bonding And Molecular Structure 111 electron pair is situated exactly between the two identical nuclei. The bond so formed is called nonpolar covalent bond. Contrary to this in case of a heteronuclear molecule like HF, the shared electron pair between the two atoms gets displaced more towards fluorine since the electronegativity of fluorine (Unit 3) is far greater than that of hydrogen. The resultant covalent bond is a polar covalent bond. As a result of polarisation, the molecule possesses the dipole moment (depicted below) which can be defined as the product of the magnitude of the charge and the distance between the centres of positive and negative charge. It is usually designated by a Greek letter 'μ'. Mathematically, it is expressed as follows : Dipole moment (μ) = charge (Q) × distance of separation (r) Dipole moment is usually expressed in Debye units (D). The conversion factor is 1 D = $3.33564 \times 10^{-30}$ C m where C is coulomb and m is meter. Further dipole moment is a vector quantity and by convention it is depicted by a small arrow with tail on the negative centre and head pointing towards the positive centre. But in chemistry presence of dipole moment is represented by the crossed arrow ( ) put on Lewis structure of the molecule. The cross is on positive end and arrow head is on negative end. For example the dipole moment of HF may be represented as : This arrow symbolises the direction of the shift of electron density in the molecule. Note that the direction of crossed arrow is opposite to the conventional direction of dipole moment vector. H F In case of polyatomic molecules the dipole moment not only depend upon the individual dipole moments of bonds known as bond dipoles but also on the spatial arrangement of various bonds in the molecule. In such case, the dipole moment of a molecule is the vector sum of the dipole moments of various bonds. For example in $H_2O$ molecule, which has a bent structure, the two O–H bonds are oriented at an angle of $104.5^0$. Net dipole moment of $6.17 \times 10^{-30}$ C m (1D = $3.33564 \times 10^{-30}$ C m) is the resultant of the dipole moments of two O–H bonds. Net Dipole moment, μ = 1.85 D = $1.85 \times 3.33564 \times 10^{-30}$C m = $6.17 \times 10^{-30}$ C m The dipole moment in case of $BeF_2$ is zero. This is because the two equal bond dipoles point in opposite directions and cancel the effect of each other. In tetra-atomic molecule, for example in $BF_3$, the dipole moment is zero although the B – F bonds are oriented at an angle of $120^o$ to one another, the three bond moments give a net sum of zero as the resultant of any two is equal and opposite to the third. Let us study an interesting case of $NH_3$ and $NF_3$ molecule. Both the molecules have pyramidal shape with a lone pair of electrons on nitrogen

atom. Although fluorine is more electronegative than nitrogen, the resultant Peter Debye, the Dutch chemist received Nobel prize in 1936 for his work on X-ray diffraction and dipole moments. The magnitude of the dipole moment is given in Debye units in order to honour him. Rationalised 2023-24 112 chemistry dipole moment of $NH_3$ ($4.90 \times 10{-}30$ C m) is greater than that of $NF_3$ ($0.8 \times 10{-}30$ C m). This is because, in case of $NH_3$ the orbital dipole due to lone pair is in the same direction as the resultant dipole moment of the N – H bonds, whereas in $NF_3$ the orbital dipole is in the direction opposite to the resultant dipole moment of the three N–F bonds. The orbital dipole because of lone pair decreases the effect of the resultant N – F bond moments, which results in the low dipole moment of $NF_3$ as represented below : • The smaller the size of the cation and the larger the size of the anion, the greater the covalent character of an ionic bond. • The greater the charge on the cation, the greater the covalent character of the ionic bond. • For cations of the same size and charge, the one, with electronic configuration $(n-1)d^nns^o$ , typical of transition metals, is more polarising than the one with a noble gas configuration, $ns^2 np^6$, typical of alkali and alkaline earth metal cations. The cation polarises the anion, pulling the electronic charge toward itself and thereby increasing the electronic charge between the two. This is precisely what happens in a covalent bond, i.e., buildup of electron charge density between the nuclei. The polarising power of the cation, the polarisability of the anion and the extent of distortion (polarisation) of anion are the factors, which determine the per cent covalent character of the ionic bond. 4.4 The Valence Shell Electron Pair Repulsion (VSEPR) Theory As already explained, Lewis concept is unable to explain the shapes of molecules. This theory provides a simple procedure to predict the shapes of covalent molecules. Sidgwick Dipole moments of some molecules are shown in Table 4.5. Just as all the covalent bonds have some partial ionic character, the ionic bonds also have partial covalent character. The partial covalent character of ionic bonds was discussed by Fajans in terms of the following rules: Table 4.5 Dipole Moments of Selected Molecules Type of Molecule Example Dipole Moment, μ(D) Geometry Molecule (AB) HF HCl HBr Hl $H_2$ 1.78 1.07 0.79 0.38 0 linear linear linear linear linear Molecule (AB2) $H_2O$ $H_2S$ $CO_2$ 1.85 0.95 0 bent bent linear Molecule (AB3) $NH_3$ $NF_3$ $BF_3$ 1.47 0.23 0 trigonal-pyramidal trigonal-pyramidal trigonal-planar Molecule (AB4) $CH_4$ $CHCl_3$ $CCl_4$ 0 1.04 0 tetrahedral tetrahedral tetrahedral Rationalised 2023-24 Chemical Bonding And Molecular Structure 113 and Powell in 1940, proposed a simple theory based on the repulsive interactions of the electron pairs in the valence shell of the atoms. It was further developed and redefined by Nyholm and Gillespie (1957). The main postulates of VSEPR theory are as follows: • The shape of a molecule depends upon the number of valence shell electron pairs (bonded or nonbonded) around the central atom. • Pairs of electrons in the valence shell repel one another since their electron clouds are negatively charged. • These pairs of electrons tend to occupy such positions in space that minimise repulsion and thus maximise distance between them. • The valence shell is taken as a sphere with the electron pairs localising on the spherical surface at maximum distance from one another. • A multiple bond is treated as if it is a single electron pair and the two or three electron pairs of a multiple bond are treated as a single super pair. • Where two or more resonance structures can represent a molecule, the VSEPR model is applicable to any such structure. The repulsive interaction of electron pairs decrease in the order: Lone pair (lp) – Lone pair (lp) > Lone pair (lp) – Bond pair (bp) > Bond pair (bp) – Bond pair (bp) Nyholm and Gillespie (1957) refined the VSEPR model by explaining the important difference between the lone pairs and bonding pairs of electrons. While the lone pairs are localised on the central atom, each bonded pair is shared between two atoms. As a result, the lone pair electrons in a molecule occupy more space as compared to the bonding pairs of electrons. This results in greater repulsion between lone pairs of electrons as compared to the lone pair - bond pair and bond pair - bond pair repulsions. These repulsion effects result in deviations from idealised shapes and alterations in bond angles in molecules. For the prediction of geometrical shapes of molecules with the help of VSEPR theory, it is convenient to divide molecules into two categories as

(i) molecules in which the central atom has no lone pair and (ii) molecules in which the central atom has one or more lone pairs. Table 4.6 (page114) shows the arrangement of electron pairs about a central atom A (without any lone pairs) and geometries of some molecules/ions of the type AB. Table 4.7 (page 115) shows shapes of some simple molecules and ions in which the central atom has one or more lone pairs. Table 4.8 (page 116) explains the reasons for the distortions in the geometry of the molecule. A s depicted in Table 4.6, in the compounds of AB2, AB3, AB4, AB5 and AB6, the arrangement of electron pairs and the B atoms around the central atom A are : linear, trigonal planar, tetrahedral, trigonal-bipyramidal and octahedral, respectively. Such arrangement can be seen in the molecules like BF3 (AB3), CH4 (AB4) and PCl5 (AB5) as depicted below by their ball and stick models. The VSEPR Theory is able to predict geometry of a large number of molecules, especially the compounds of p-block elements accurately. It is also quite successful in determining the geometry quite-accurately even when the energy difference between possible structures is very small. The theoretical basis ofthe VSEPR theory regarding the effects of electron pair repulsions on molecular shapes is not clear and continues to be a subject of doubt and discussion. Fig. 4.6 The shapes of molecules in which central atom has no lone pair Rationalised 2023-24 114 chemistry Table 4.6 Geometry of Molecules in which the Central Atom has No Lone Pair of Electrons Rationalised 2023-24 Chemical Bonding And Molecular Structure 115 Table 4.7 Shape (geometry) of Some Simple Molecules/Ions with Central Ions having One or More Lone Pairs of Electrons(E). Rationalised 2023-24 116 chemistry Theoretically the shape should have been triangular planar but actually it is found to be bent or v-shaped. The reason being the lone pairbond pair repulsion is much more as compared to the bond pair-bond pair repulsion. So the angle is reduced to 119.5° from 120°. Had there been a bp in place of lp the shape would have been tetrahedral but one lone pair is present and due to the repulsion between lp-bp (which is more than bp-bp repulsion) the angle between bond pairs is reduced to 107° from 109.5°. The shape should have been tetrahedral if there were all bp but two lp are present so the shape is distorted tetrahedral or angular. The reason is lp-lp repulsion is more than lp-bp repulsion which is more than bp-bp repulsion. Thus, the angle is reduced to 104.5° from 109.5°. Bent Trigonal pyramidal Bent AB2E 4 1 AB3E 3 1 AB2E2 2 2 In (a) the lp is present at axial position so there are three lp—bp repulsions at 90°. In(b) the lp is in an equatorial position, and there are two lp—bp repulsions. Hence, arrangement (b) is more stable. The shape shown in (b) is described as a distorted tetrahedron, a folded square or a see-saw. Seesaw AB4E 4 1 (More stable) Table 4.8 Shapes of Molecules containing Bond Pair and Lone Pair Shape Reason for the shape acquired Arrangement of electrons No. of lone pairs No. of bonding pairs Molecule type Rationalised 2023-24 Chemical Bonding And Molecular Structure 117 In (a) the lp are at equatorial position so there are less lpbp repulsions as compared to others in which the lp are at axial positions. So structure (a) is most stable. (T-shaped). AB T-shape 3E2 3 2 Shape Reason for the shape acquired Arrangement of electrons No. of lone pairs No. of bonding pairs Molecule type 4.5 Valence Bond Theory As we know that Lewis approach helps in writing the structure of molecules but it fails to explain the formation of chemical bond. It also does not give any reason for the difference in bond dissociation enthalpies and bond lengths in molecules like H2 (435.8 kJ mol-1, 74 pm) and F2 (155 kJ mol-1, 144 pm), although in both the cases a single covalent bond is formed by the sharing of an electron pair between the respective atoms. It also gives no idea about the shapes of polyatomic molecules. Similarly the VSEPR theory gives the geometry of simple molecules but theoretically, it does not explain them and also it has limited applications. To overcome these limitations the two important theories based on quantum mechanical principles are introduced. These are valence bond (VB) theory and molecular orbital (MO) theory. Valence bond theory was introduced by Heitler and London (1927) and developed further by Pauling and others. A discussion of the valence bond theory is based on the knowledge of atomic orbitals, electronic configurations of elements (Units 2), the overlap criteria of atomic orbitals, the hybridization of atomic orbitals and the

principles of variation and superposition. A rigorous treatment of the VB theory in terms of these aspects is beyond the scope of this book. Therefore, for the sake of convenience, valence bond theory has been discussed in terms of qualitative and non-mathematical treatment only. To start with, let us consider the formation of hydrogen molecule which is the simplest of all molecules. Consider two hydrogen atoms A and B approaching each other having nuclei NA and NB and electrons present in them are represented by eA and eB. When the two atoms are at large distance from each other, there is no interaction between them. As these two atoms approach each other, new attractive and repulsive forces begin to operate. Attractive forces arise between: (i) nucleus of one atom and its own electron that is NA – eA and NB– eB. Rationalised 2023-24 118 chemistry (ii) nucleus of one atom and electron of other atom i.e., NA– eB, NB– eA. Similarly repulsive forces arise between (i) electrons of two atoms like eA – eB, (ii) nuclei of two atoms NA – NB. Attractive forces tend to bring the two atoms close to each other whereas repulsive forces tend to push them apart (Fig. 4.7). Experimentally it has been found that the magnitude of new attractive force is more than the new repulsive forces. As a result, two atoms approach each other and potential energy decreases. Ultimately a stage is reached where the net force of attraction balances the force of repulsion and system acquires minimum energy. At this stage two hydrogen atoms are said to be bonded Fig. 4.7 Forces of attraction and repulsion during the formation of H2 molecule together to form a stable molecule having the bond length of 74 pm. Since the energy gets released when the bond is formed between two hydrogen atoms, the hydrogen molecule is more stable than that of isolated hydrogen atoms. The energy so released is called as bond enthalpy, which is corresponding to minimum in the curve depicted in Fig. 4.8. Conversely, 435.8 kJ of energy is required to dissociate one mole of H2 molecule. H2(g) + 435.8 kJ mol–1 → H(g) + H(g) 4.5.1 Orbital Overlap Concept In the formation of hydrogen molecule, there is a minimum energy state when two hydrogen atoms are so near that their atomic orbitals undergo partial interpenetration. This partial merging of atomic orbitals is called overlapping of atomic orbitals which results in the pairing of electrons. The extent of overlap decides the strength of a covalent bond. In general, greater the overlap the stronger is the bond formed between two atoms. Therefore, according to orbital overlap concept, the formation of a covalent bond between two atoms results by pairing of electrons present in the valence shell having opposite spins. Fig. 4.8 The potential energy curve for the formation of H2 molecule as a function of internuclear distance of the H atoms. The minimum in the curve corresponds to the most stable state of H2. Rationalised 2023-24 Chemical Bonding And Molecular Structure 119 4.5.2 Directional Properties of Bonds As we have already seen, the covalent bond is formed by overlapping of atomic orbitals. The molecule of hydrogen is formed due to the overlap of 1s-orbitals of two H atoms. In case of polyatomic molecules like CH4, NH3 and H2O, the geometry of the molecules is also important in addition to the bond formation. For example why is it so that CH4 molecule has tetrahedral shape and HCH bond angles are 109.5°? Why is the shape of NH3 molecule pyramidal ? The valence bond theory explains the shape, the formation and directional properties of bonds in polyatomic molecules like CH4, NH3 and H2O, etc. in terms of overlap and hybridisation of atomic orbitals. 4.5.3 Overlapping of Atomic Orbitals When orbitals of two atoms come close to form bond, their overlap may be positive, negative or zero depending upon the sign (phase) and direction of orientation of amplitude of orbital wave function in space (Fig. 4.9). Positive and negative sign on boundary surface diagrams in the Fig. 4.9 show the sign (phase) of orbital wave function and are not related to charge. Orbitals forming bond should have same sign (phase) and orientation in space. This is called positive overlap. Various overlaps of s and p orbitals are depicted in Fig. 4.9. The criterion of overlap, as the main factor for the formation of covalent bonds applies uniformly to the homonuclear/heteronuclear diatomic molecules and polyatomic molecules. We know that the shapes of CH4, NH3, and H2O molecules are tetrahedral, pyramidal and bent respectively. It would be therefore interesting to use VB theory to find out if these geometrical shapes can be explained in

terms of the orbital overlaps. Let us first consider the CH4 (methane) molecule. The electronic configuration of carbon in its ground state is [He]2s2 2p2 which in the excited state becomes [He] 2s1 2px 1 2py 1 2pz 1. The energy required for this excitation is compensated by the release of energy due to overlap between the orbitals of carbon and the Fig.4.9 Positive, negative and zero overlaps of s and p atomic orbitals hydrogen. The four atomic orbitals of carbon, each with an unpaired electron can overlap with the 1s orbitals of the four H atoms which are also singly occupied. This will result in the formation of four C-H bonds. It will, however, be observed that while the three p orbitals of carbon are at 90° to one another, the HCH angle for these will also be 90° . That is three C-H bonds will be oriented at 90° to one another. The 2s orbital of carbon and the 1s orbital of H are spherically symmetrical and they can overlap in any direction. Therefore the direction of the fourth C-H bond cannot be ascertained. This description does not fit in with the tetrahedral HCH angles of 109.5° . Clearly, it follows that simple atomic orbital overlap does not account for the directional characteristics of bonds in CH4. Using similar procedure and arguments, it can be seen that in the case of NH3 and H2O molecules, the HNH Rationalised 2023-24 120 chemistry and HOH angles should be 90° . This is in disagreement with the actual bond angles of 107° and 104.5° in the NH3 and H2O molecules respectively. 4.5.4 Types of Overlapping and Nature of Covalent Bonds The covalent bond may be classified into two types depending upon the types of overlapping: (i) Sigma(σ) bond, and (ii) pi(π) bond (i) Sigma(σ) bond : This type of covalent bond is formed by the end to end (headon) overlap of bonding orbitals along the internuclear axis. This is called as head on overlap or axial overlap. This can be formed by any one of the following types of combinations of atomic orbitals. • s-s overlapping : In this case, there is overlap of two half filled s-orbitals along the internuclear axis as shown below : • s-p overlapping: This type of overlap occurs between half filled s-orbitals of one atom and half filled p-orbitals of another atom. • p–p overlapping : This type of overlap takes place between half filled p-orbitals of the two approaching atoms. (ii) pi( ) bond : In the formation of π bond the atomic orbitals overlap in such a way that their axes remain parallel to each other and perpendicular to the internuclear axis. The orbitals formed due to sidewise overlapping consists of two saucer type charged clouds above and below the plane of the participating atoms. 4.5.5 Strength of Sigma and pi Bonds Basically the strength of a bond depends upon the extent of overlapping. In case of sigma bond, the overlapping of orbitals takes place to a larger extent. Hence, it is stronger as compared to the pi bond where the extent of overlapping occurs to a smaller extent. Further, it is important to note that in the formation of multiple bonds between two atoms of a molecule, pi bond(s) is formed in addition to a sigma bond. 4.6 Hybridisation In order to explain the characteristic geometrical shapes of polyatomic molecules like CH4, NH3 and H2O etc., Pauling introduced the concept of hybridisation. According to him the atomic orbitals combine to form new set of equivalent orbitals known as hybrid orbitals. Unlike pure orbitals, the hybrid orbitals are used in bond formation. The phenomenon is known as hybridisation which can be defined as the process of intermixing of the orbitals of slightly different energies so as to redistribute their energies, resulting in the formation of new set of orbitals of equivalent energies and shape. For example when one 2s and three 2p-orbitals of carbon hybridise, there is the formation of four new sp3 hybrid orbitals. Salient features of hybridisation: The main features of hybridisation are as under : 1. The number of hybrid orbitals is equal to the number of the atomic orbitals that get hybridised. 2. The hybridised orbitals are always equivalent in energy and shape. Rationalised 2023-24 Chemical Bonding And Molecular Structure 121 3. The hybrid orbitals are more effective in forming stable bonds than the pure atomic orbitals. 4. These hybrid orbitals are directed in space in some preferred direction to have minimum repulsion between electron pairs and thus a stable arrangement. Therefore, the type of hybridisation indicates the geometry of the molecules. Important conditions for hybridisation (i) The orbitals present in the valence shell of the atom are hybridised. (ii) The orbitals undergoing hybridisation should have almost equal energy. (iii) Promotion of electron is not

essential condition prior to hybridisation. (iv) It is not necessary that only half filled orbitals participate in hybridisation. In some cases, even filled orbitals of valence shell take part in hybridisation. 4.6.1 Types of Hybridisation There are various types of hybridisation involving s, p and d orbitals. The different types of hybridisation are as under: (I) sp hybridisation: This type of hybridisation involves the mixing of one s and one p orbital resulting in the formation of two equivalent sp hybrid orbitals. The suitable orbitals for sp hybridisation are s and $p_z$, if the hybrid orbitals are to lie along the z-axis. Each sp hybrid orbitals has 50% s-character and 50% p-character. Such a molecule in which the central atom is sp-hybridised and linked directly to two other central atoms possesses linear geometry. This type of hybridisation is also known as diagonal hybridisation. The two sp hybrids point in the opposite direction along the z-axis with projecting positive lobes and very small negative lobes, which provides more effective overlapping resulting in the formation of stronger bonds. Example of molecule having sp hybridisation $BeCl_2$: The ground state electronic configuration of Be is $1s^2 2s^2$. In the exited state one of the 2s-electrons is promoted to vacant 2p orbital to account for its bivalency. One 2s and one 2p-orbital gets hybridised to form two sp hybridised orbitals. These two sp hybrid orbitals are oriented in opposite direction forming an angle of 180°. Each of the sp hybridised orbital overlaps with the 2p-orbital of chlorine axially and form two BeCl sigma bonds. This is shown in Fig. 4.10. (II) sp2 hybridisation : In this hybridisation there is involvement of one s and two p-orbitals in order to form three equivalent sp2 hybridised orbitals. For example, in $BCl_3$ molecule, the ground state electronic configuration of central boron atom is $1s^2 2s^2 2p^1$. In the excited state, one of the 2s electrons is promoted to vacant 2p orbital as Fig.4.10 (a) Formation of sp hybrids from s and p orbitals; (b) Formation of the linear $BeCl_2$ molecule Be Fig.4.11 Formation of sp2 hybrids and the $BCl_3$ molecule Rationalised 2023-24 122 chemistry a result boron has three unpaired electrons. These three orbitals (one 2s and two 2p) hybridise to form three sp2 hybrid orbitals. The three hybrid orbitals so formed are oriented in a trigonal planar arrangement and overlap with 2p orbitals of chlorine to form three B-Cl bonds. Therefore, in $BCl_3$ (Fig. 4.11), the geometry is trigonal planar with ClBCl bond angle of 120°. (III) sp3 hybridisation: This type o f hybridisation can be explained by taking the example of $CH_4$ molecule in which there is mixing of one s-orbital and three p-orbitals of the valence shell to form four sp3 hybrid orbital of equivalent energies and shape. There is 25% s-character and 75% p-character in each sp3 hybrid orbital. The four sp3 hybrid orbitals so formed are directed towards the four corners of the tetrahedron. The angle between sp3 hybrid orbital is 109.5° as shown in Fig. 4.12. Fig.4.12 Formation of sp3 hybrids by the combination of s, $p_x$, $p_y$ and $p_z$ atomic orbitals of carbon and the formation of $CH_4$ molecule σ σ σ σ The structure of $NH_3$ and $H_2O$ molecules can also be explained with the help of sp3 hybridisation. In $NH_3$, the valence shell (outer) electronic configuration of nitrogen in the ground state is 2 2 2 2 2 1 1 1 S $p_x$ y p $p_z$ having three unpaired electrons in the sp3 hybrid orbitals and a lone pair of electrons is present in the fourth one. These three hybrid orbitals overlap with 1s orbitals of hydrogen atoms to form three N–H sigma bonds. We know that the force of repulsion between a lone pair and a bond pair is more than the force of repulsion between two bond pairs of electrons. The molecule thus gets distorted and the bond angle is reduced to 107° from 109.5°. The geometry of such a molecule will be pyramidal as shown in Fig. 4.13. Fig.4.13 Formation of $NH_3$ molecule In case of $H_2O$ molecule, the four oxygen orbitals (one 2s and three 2p) undergo sp3 hybridisation forming four sp3 hybrid orbitals out of which two contain one electron each and the other two contain a pair of electrons. These four sp3 hybrid orbitals acquire a tetrahedral geometry, with two corners occupied by hydrogen atoms while the other two by the lone pairs. The bond angle in this case is reduced to 104.5° from 109.5° (Fig. 4.14) and the molecule thus acquires a V-shape or angular geometry. Fig.4.14 Formation of $H_2O$ molecule Rationalised 2023-24 Chemical Bonding And Molecular Structure 123 4.6.2 Other Examples of sp3, sp2 and sp Hybridisation sp3 Hybridisation in $C_2H_6$ molecule: In ethane molecule both the carbon atoms assume sp3 hybrid state. One of the four

sp3 hybrid orbitals of carbon atom overlaps axially with similar orbitals of other atom to form sp3-sp3 sigma bond while the other three hybrid orbitals of each carbon atom are used in forming sp3–s sigma bonds with hydrogen atoms as discussed in section 4.6.1(iii). Therefore in ethane C–C bond length is 154 pm and each C–H bond length is 109 pm. sp2 Hybridisation in C2H4: In the formation of ethene molecule, one of the sp2 hybrid orbitals of carbon atom overlaps axially with sp2 hybridised orbital of another carbon atom to form C–C sigma bond. While the other two sp2 hybrid orbitals of each carbon atom are used for making sp2–s sigma bond with two hydrogen atoms. The unhybridised orbital (2px or 2py) of one carbon atom overlaps sidewise with the similar orbital of the other carbon atom to form weak π bond, which consists of two equal electron clouds distributed above and below the plane of carbon and hydrogen atoms. Thus, in ethene molecule, the carboncarbon bond consists of one sp2–sp2 sigma bond and one pi (π ) bond between p orbitals which are not used in the hybridisation and are perpendicular to the plane of molecule; the bond length 134 pm. The C–H bond is sp2–s sigma with bond length 108 pm. The H–C–H bond angle is 117.6° while the H–C–C angle is 121°. The formation of sigma and pi bonds in ethene is shown in Fig. 4.15. Fig. 4.15 Formation of sigma and pi bonds in ethene Rationalised 2023-24 124 chemistry sp Hybridisation in C2H2 : In the formation of ethyne molecule, both the carbon atoms undergo sp-hybridisation having two unhybridised orbital i.e., 2py and 2px . One sp hybrid orbital of one carbon atom overlaps axially with sp hybrid orbital of the other carbon atom to form C–C sigma bond, while the other hybridised orbital of each carbon atom overlaps axially with the half filled s orbital of hydrogen atoms forming σ bonds. Each of the two unhybridised p orbitals of both the carbon atoms overlaps sidewise to form two π bonds between the carbon atoms. So the triple bond between the two carbon atoms is made up of one sigma and two pi bonds as shown in Fig. 4.16. 4.6.3 Hybridisation of Elements involving d Orbitals The elements present in the third period contain d orbitals in addition to s and p orbitals. The energy of the 3d orbitals are comparable to the energy of the 3s and 3p orbitals. The energy of 3d orbitals are also comparable to those of 4s and 4p orbitals. As a consequence the hybridisation involving either 3s, 3p and 3d or 3d, 4s and 4p is possible. However, since the difference in energies of 3p and 4s orbitals is significant, no hybridisation involving 3p, 3d and 4s orbitals is possible. The important hybridisation schemes involving s, p and d orbitals are summarised below: Fig.4.16 Formation of sigma and pi bonds in ethyne (i) Formation of PCl5 (sp3d hybridisation): The ground state and the excited state outer electronic configurations of phosphorus (Z=15) are represented below. sp3d hybrid orbitals filled by electron pairs donated by five Cl atoms.

| Shape of molecules/ ions | Hybridisation type | Atomic orbitals | Examples |
| --- | --- | --- | --- |
| Square planar | dsp2 | d+s+p(2) | [Ni(CN)4] 2–, [Pt(Cl)4] 2– |
| Trigonal bipyramidal | sp3d | s+p(3)+d | PF5, PCl5 |
| Square pyramidal | sp3d2 | s+p(3)+d(2) | BrF5 |
| Octahedral | sp3d2 d2sp3 | s+p(3)+d(2) d(2)+s+p(3) | SF6, [CrF6] 3– [Co(NH3) 6] 3+ |

Rationalised 2023-24 Chemical Bonding And Molecular Structure 125 Now the five orbitals (i.e., one s, three p and one d orbitals) are available for hybridisation to yield a set of five sp3d hybrid orbitals which are directed towards the five corners of a trigonal bipyramidal as depicted in the Fig. 4.17. Fig. 4.17 Trigonal bipyramidal geometry of PCl5 molecule It should be noted that all the bond angles in trigonal bipyramidal geometry are not equivalent. In PCl5 the five sp3d orbitals of phosphorus overlap with the singly occupied p orbitals of chlorine atoms to form five P–Cl sigma bonds. Three P–Cl bond lie in one plane and make an angle of 120° with each other; these bonds are termed as equatorial bonds. The remaining two P–Cl bonds–one lying above and the other lying below the equatorial plane, make an angle of 90° with the plane. These bonds are called axial bonds. As the axial bond pairs suffer more repulsive interaction from the equatorial bond pairs, therefore axial bonds have been found to be slightly longer and hence slightly weaker than the equatorial bonds; which makes PCl5 molecule more reactive. (ii) Formation of SF6 (sp3d2 hybridisation): In SF6 the central sulphur atom has the ground state outer electronic configuration 3s23p4. In the exited state the available six orbitals i.e., one s, three p and two d are singly occupied by electrons. These

orbitals hybridise to form six new sp3d2 hybrid orbitals, which are projected towards the six corners of a regular octahedron in SF6. These six sp3d2 hybrid orbitals overlap with singly occupied orbitals of fluorine atoms to form six S–F sigma bonds. Thus SF6 molecule has a regular octahedral geometry as shown in Fig. 4.18. sp3d2 hybridisation 4.7 Molecular Orbital Theory Molecular orbital (MO) theory was developed by F. Hund and R.S. Mulliken in 1932. The salient features of this theory are : (i) The electrons in a molecule are present in the various molecular orbitals as the electrons of atoms are present in the various atomic orbitals. (ii) The atomic orbitals of comparable energies and proper symmetry combine to form molecular orbitals. (iii) While an electron in an atomic orbital is influenced by one nucleus, in a molecular orbital it is influenced by two or more nuclei depending upon the number of atoms in the molecule. Thus, Fig. 4.18 Octahedral geometry of SF6 molecule Rationalised 2023-24 126 chemistry an atomic orbital is monocentric while a molecular orbital is polycentric. (iv) The number of molecular orbital formed is equal to the number of combining atomic orbitals. When two atomic orbitals combine, two molecular orbitals are formed. One is known as bonding molecular orbital while the other is called antibonding molecular orbital. (v) The bonding molecular orbital has lower energy and hence greater stability than the corresponding antibonding molecular orbital. (vi) Jus t as the electron probability distribution around a nucleus in an atom is given by an atomic orbital, the electron probability distribution around a group of nuclei in a molecule is given by a molecular orbital. (vii) The molecular orbitals like atomic orbitals are filled in accordance with the aufbau principle obeying the Pauli's exclusion principle and the Hund's rule. 4.7.1 Formation of Molecular Orbitals Linear Combination of Atomic Orbitals (LCAO) According to wave mechanics, the atomic orbitals can be expressed by wave functions ($\psi$ 's) which represent the amplitude of the electron waves. These are obtained from the solution of Schrödinger wave equation. However, since it cannot be solved for any system containing more than one electron, molecular orbitals which are one electron wave functions for molecules are difficult to obtain directly from the solution of Schrödinger wave equation. To overcome this problem, an approximate method known as linear combination of atomic orbitals (LCAO) has been adopted. Let u s apply this method to the homonuclear diatomic hydrogen molecule. Consider the hydrogen molecule consisting of two atoms A and B. Each hydrogen atom in the ground state has one electron in 1s orbital. The atomic orbitals of these atoms may be represented by the wave functions $\psi_A$ and $\psi_B$. Mathematically, the formation of molecular orbitals may be described by the linear combination of atomic orbitals that can take place by addition and by subtraction of wave functions of individual atomic orbitals as shown below : $\psi_{MO} = \psi_A + \psi_B$ Therefore, the two molecular orbitals $\sigma$ and $\sigma^*$ are formed as : $\sigma = \psi_A + \psi_B$ $\sigma^* = \psi_A - \psi_B$ The molecular orbital $\sigma$ formed by the addition of atomic orbitals is called the bonding molecular orbital while the molecular orbital $\sigma^*$ formed by the subtraction of atomic orbital is called antibonding molecular orbital as depicted in Fig. 4.19. Fig.4.19 Formation of bonding ($\sigma$) and antibonding ($\sigma^*$) molecular orbitals by the linear combination of atomic orbitals $\psi_A$ and $\psi_B$ centered on two atoms A and B respectively. Qualitatively, the formation of molecular orbitals can be understood in terms of the constructive or destructive interference of the electron waves of the combining atoms. In the formation of bonding molecular orbital, the two electron waves of the bonding atoms reinforce each other due to constructive interference while in the formation of $\sigma^* = \psi_A - \psi_B$ $\psi_A$ $\psi_B$ $\sigma = \psi_A + \psi_B$ Rationalised 2023-24 Chemical Bonding And Molecular Structure 127 antibonding molecular orbital, the electron waves cancel each other due to destructive interference. As a result, the electron density in a bonding molecular orbital is located between the nuclei of the bonded atoms because of which the repulsion between the nuclei is very less while in case of an antibonding molecular orbital, most of the electron density is located away from the space between the nuclei. Infact, there is a nodal plane (on which the electron density is zero) between the nuclei and hence the repulsion between the nuclei is high. Electrons placed in a bonding molecular orbital tend to hold the nuclei together and stabilise a molecule. Therefore, a bonding molecular orbital

always possesses lower energy than either of the atomic orbitals that have combined to form it. In contrast, the electrons placed in the antibonding molecular orbital destabilise the molecule. This is because the mutual repulsion of the electrons in this orbital is more than the attraction between the electrons and the nuclei, which causes a net increase in energy. It may be noted that the energy of the antibonding orbital is raised above the energy of the parent atomic orbitals that have combined and the energy of the bonding orbital has been lowered than the parent orbitals. The total energy of two molecular orbitals, however, remains the same as that of two original atomic orbitals. 4.7.2 Conditions for the Combination of Atomic Orbitals The linear combination of atomic orbitals to form molecular orbitals takes place only if the following conditions are satisfied: 1. The combining atomic orbitals must have the same or nearly the same energy. This means that 1s orbital can combine with another 1s orbital but not with 2s orbital because the energy of 2s orbital is appreciably higher than that of 1s orbital. This is not true if the atoms are very different. 2. The combining atomic orbitals must have the same symmetry about the molecular axis. By convention z-axis is taken as the molecular axis. It is important to note that atomic orbitals having same or nearly the same energy will not combine if they do not have the same symmetry. For example, 2pz orbital of one atom can combine with 2pz orbital of the other atom but not with the 2px or 2py orbitals because of their different symmetries. 3. The combining atomic orbitals must overlap to the maximum extent. Greater the extent of overlap, the greater will be the electron-density between the nuclei of a molecular orbital. 4.7.3 Types of Molecular Orbitals Molecular orbitals of diatomic molecules are designated as σ (sigma), π (pi), δ (delta), etc. In this nomenclature, the sigma ( ) molecular orbitals are symmetrical around the bond-axis while pi ( ) molecular orbitals are not symmetrical. For example, the linear combination of 1s orbitals centered on two nuclei produces two molecular orbitals which are symmetrical around the bond-axis. Such molecular orbitals are of the σ type and are designated as σ1s and σ*1s [Fig. 4.20(a), page 124]. If internuclear axis is taken to be in the z-direction, it can be seen that a linear combination of 2pz - orbitals of two atoms also produces two sigma molecular orbitals designated as 2pz and *2pz . [Fig. 4.20(b)] Molecular orbitals obtained from 2px and 2py orbitals are not symmetrical around the bond axis because of the presence of positive lobes above and negative lobes below the molecular plane. Such molecular orbitals, are labelled as π and =π * [Fig. 4.20(c)]. A π bonding MO has larger electron density above and below the inter-nuclear axis. The π* antibonding MO has a node between the nuclei. 4.7.4 Energy Level Diagram for Molecular Orbitals We have seen that 1s atomic orbitals on two atoms form two molecular orbitals designated as σ1s and σ*1s. In the same manner, the 2s and 2p atomic orbitals (eight atomic orbitals Rationalised 2023-24 128 chemistry Fig. 4.20 Contours and energies of bonding and antibonding molecular orbitals formed through combinations of (a) 1s atomic orbitals; (b) 2pz atomic orbitals and (c) 2px atomic orbitals. on two atoms) give rise to the following eight molecular orbitals: Antibonding MOs σ∗2s σ∗2pz π∗2px π∗2py Bonding MOs σ2s σ2pz π2px π2py The energy levels of these molecular orbitals have been determined experimentally from spectroscopic data for homonuclear diatomic molecules of second row elements of the periodic table. The increasing order of Rationalised 2023-24 Chemical Bonding And Molecular Structure 129 energies of various molecular orbitals for O2 and F2 is given below: 1s < ∗1s <  2s < ∗2s < 2pz < (π 2px =π 2py) < (π∗2px = π∗ 2py) < ∗2pz However, this sequence of energy levels of molecular orbitals is not correct for the remaining molecules Li2, Be2, B2, C2, N2. For instance, it has been observed experimentally that for molecules such as B2, C2, N2, etc. the increasing order of energies of various molecular orbitals is 1s < ∗1s < 2s < ∗2s < (π 2 px = π 2 py) < 2pz < (π∗2px =π∗2py) < ∗2pz The important characteristic feature of this order is that the energy of 2pz molecular orbital is higher than that of 2px and 2py molecular orbitals. 4.7.5 Electronic Configuration and Molecular Behaviour The distribution of electrons among various molecular orbitals is called the electronic configuration of the molecule. From the electronic configuration of the molecule, it is possible to get important

information about the molecule as discussed below. Stability of Molecules: If Nb is the number of electrons occupying bonding orbitals and Na the number occupying the antibonding orbitals, then (i) the molecule is stable if Nb is greater than Na, and (ii) the molecule is unstable if Nb is less than Na. In (i) more bonding orbitals are occupied and so the bonding influence is stronger and a stable molecule results. In (ii) the antibonding influence is stronger and therefore the molecule is unstable. Bond order Bond order (b.o.) is defined as one half the difference between the number of electrons present in the bonding and the antibonding orbitals i.e., Bond order (b.o.) = ½ (Nb–Na) The rules discussed above regarding the stability of the molecule can be restated in terms of bond order as follows: A positive bond order (i.e., Nb > Na) means a stable molecule while a negative (i.e., Nb lp-bp > bp-bp The valence bond (VB) approach to covalent bonding is basically concerned with the energetics of covalent bond formation about which the Lewis and VSEPR models are silent. Basically the VB theory discusses bond formation in terms of overlap of orbitals. For example the formation of the H2 molecule from two hydrogen atoms involves the overlap of the 1s orbitals of the two H atoms which are singly occupied. It is seen that the potential energy of the system gets lowered as the two H atoms come near to each other. At the equilibrium inter-nuclear distance (bond distance) the energy touches a minimum. Any attempt to bring the nuclei still closer results in a sudden increase in energy and consequent destabilization of the molecule. Because of orbital overlap the electron density between the nuclei increases which helps in bringing them closer. It is however seen that the actual bond enthalpy and bond length values are not obtained by overlap alone and other variables have to be taken into account. For explaining the characteristic shapes of polyatomic molecules Pauling introduced the concept of hybridisation of atomic orbitals. sp, sp2, sp3 hybridizations of atomic orbitals of Be, B, C, N and O are used to explain the formation and geometrical shapes of molecules like BeCl2, BCl3, CH4, NH3 and H2O. They also explain the formation of multiple bonds in molecules like C2H2 and C2H4. The molecular orbital (MO) theory describes bonding in terms of the combination and arrangment of atomic orbitals to form molecular orbitals that are associated with the molecule as a whole. The number of molecular orbitals are always equal to the number of atomic orbitals from which they are formed. Bonding molecular orbitals increase electron density between the nuclei and are lower in energy than the individual atomic orbitals. Antibonding molecular orbitals have a region of zero electron density between the nuclei and have more energy than the individual atomic orbitals. The electronic configuration of the molecules is written by filling electrons in the molecular orbitals in the order of increasing energy levels. As in the case of atoms, the Pauli exclusion principle and Hund's rule are applicable for the filling of molecular orbitals. Molecules are said to be stable if the number of elctrons in bonding molecular orbitals is greater than that in antibonding molecular orbitals. Hydrogen bond is formed when a hydrogen atom finds itself between two highly electronegative atoms such as F, O and N. It may be intermolecular (existing between two or more molecules of the same or different substances) or intramolecular (present within the same molecule). Hydrogen bonds have a powerful effect on the structure and properties of many compounds. EXERCISES 4.1 Explain the formation of a chemical bond. 4.2 Write Lewis dot symbols for atoms of the following elements : Mg, Na, B, O, N, Br. 4.3 Write Lewis symbols for the following atoms and ions: S and S2–; Al and Al3+; H and H– 4.4 Draw the Lewis structures for the following molecules and ions : H2S, SiCl4, BeF2, CO3 2– , HCOOH 4.5 Define octet rule. Write its significance and limitations. Rationalised 2023-24 134 chemistry 4.6 Write the favourable factors for the formation of ionic bond. 4.7 Discuss the shape of the following molecules using the VSEPR model: BeCl2, BCl3, SiCl4, AsF5, H2S, PH3 4.8 Although geometries of NH3 and H2O molecules are distorted tetrahedral, bond angle in water is less than that of ammonia. Discuss. 4.9 How do you express the bond strength in terms of bond order ? 4.10 Define the bond length. 4.11 Explain the important aspects of resonance with reference to the CO3 2– ion. 4.12 H3PO3 can be represented by structures 1 and 2 shown below. Can these two structures be taken as the canonical forms of the

resonance hybrid representing H3PO3 ? If not, give reasons for the same. 4.13 Write the resonance structures for SO3, NO2 and NO3 − . 4.14 Use Lewis symbols to show electron transfer between the following atoms to form cations and anions : (a) K and S (b) Ca and O (c) Al and N. 4.15 Although both CO2 and H2O are triatomic molecules, the shape of H2O molecule is bent while that of CO2 is linear. Explain this on the basis of dipole moment. 4.16 Write the significance/applications of dipole moment. 4.17 Define electronegativity. How does it differ from electron gain enthalpy ? 4.18 Explain with the help of suitable example polar covalent bond. 4.19 Arrange the bonds in order of increasing ionic character in the molecules: LiF, K2O, N2, SO2 and ClF3. 4.20 The skeletal structure of CH3COOH as shown below is correct, but some of the bonds are shown incorrectly. Write the correct Lewis structure for acetic acid. 4.21 Apart from tetrahedral geometry, another possible geometry for CH4 is square planar with the four H atoms at the corners of the square and the C atom at its centre. Explain why CH4 is not square planar ? 4.22 Explain why BeH2 molecule has a zero dipole moment although the Be–H bonds are polar. 4.23 Which out of NH3 and NF3 has higher dipole moment and why ? 4.24 What is meant by hybridisation of atomic orbitals? Describe the shapes of sp, sp2, sp3 hybrid orbitals. 4.25 Describe the change in hybridisation (if any) of the Al atom in the following reaction. AlCl Cl AlCl 3 4 -☐ ☐ Rationalised 2023-24 Chemical Bonding And Molecular Structure 135 4.26 Is there any change in the hybridisation of B and N atoms as a result of the following reaction? 4.27 Draw diagrams showing the formation of a double bond and a triple bond between carbon atoms in C2H4 and C2H2 molecules. 4.28 What is the total number of sigma and pi bonds in the following molecules? (a) C2H2 (b) C2H4 4.29 Considering x-axis as the internuclear axis which out of the following will not form a sigma bond and why? (a) 1s and 1s (b) 1s and 2px ; (c) 2py and 2py (d) 1s and 2s. 4.30 Which hybrid orbitals are used by carbon atoms in the following molecules? CH3–CH3; (b) CH3–CH=CH2; (c) CH3-CH2-OH; (d) CH3-CHO (e) CH3COOH 4.31 What do you understand by bond pairs and lone pairs of electrons? Illustrate by giving one exmaple of each type. 4.32 Distinguish between a sigma and a pi bond. 4.33 Explain the formation of H2 molecule on the basis of valence bond theory. 4.34 Write the important conditions required for the linear combination of atomic orbitals to form molecular orbitals. 4.35 Use molecular orbital theory to explain why the Be2 molecule does not exist. 4.36 Compare the relative stability of the following species and indicate their magnetic properties; (superoxide), O2 2– (peroxide) 4.37 Write the significance of a plus and a minus sign shown in representing the orbitals. 4.38 Describe the hybridisation in case of PCl5. Why are the axial bonds longer as compared to equatorial bonds? 4.39 Define hydrogen bond. Is it weaker or stronger than the van der Waals forces? 4.40 What is meant by the term bond order? Calculate the bond order of : N2, O2, O2 + and O2 − . Rationalised 2023-24Thermodynamics It is the only physical theory of universal content concerning which I am convinced that, within the framework of the applicability of its basic concepts, it will never be overthrown. Albert Einstein Chemical energy stored by molecules can be released as heat during chemical reactions when a fuel like methane, cooking gas or coal burns in air. The chemical energy may also be used to do mechanical work when a fuel burns in an engine or to provide electrical energy through a galvanic cell like dry cell. Thus, various forms of energy are interrelated and under certain conditions, these may be transformed from one form into another. The study of these energy transformations forms the subject matter of thermodynamics. The laws of thermodynamics deal with energy changes of macroscopic systems involving a large number of molecules rather than microscopic systems containing a few molecules. Thermodynamics is not concerned about how and at what rate these energy transformations are carried out, but is based on initial and final states of a system undergoing the change. Laws of thermodynamics apply only when a system is in equilibrium or moves from one equilibrium state to another equilibrium state. Macroscopic properties like pressure and temperature do not change with time for a system in equilibrium state. In this unit, we would like to answer some of the important questions through thermodynamics, like: How do we determine the energy changes involved in a

chemical reaction/process? Will it occur or not? What drives a chemical reaction/process? To what extent do the chemical reactions proceed? Unit 5 After studying this Unit, you will be able to • explain the terms : system and surroundings; • discriminate between close, open and isolated systems; • explain internal energy, work and heat; • state first law of thermodynamics and express it mathematically; • calculate energy changes as work and heat contributions in chemical systems; • explain state functions: U, H. • correlate ΔU and ΔH; • measure experimentally ΔU and ΔH; • define standard states for ΔH; • calculate enthalpy changes for various types of reactions; • state and apply Hess's law of constant heat summation; • differentiate between extensive and intensive properties; • define spontaneous and nonspontaneous processes; • explain entropy a s a thermodynamic state function and apply it for spontaneity; • explain Gibbs energy change (ΔG); and • establish relationship between ΔG and spontaneity, ΔG and equilibrium constant. Rationalised 2023-24 THERMODYNAMICS 137 5.1 Thermodynamic terms We are interested in chemical reactions and the energy changes accompanying them. For this we need to know certain thermodynamic terms. These are discussed below. 5.1.1 The System and the Surroundings A system in thermodynamics refers to that part of universe in which observations are made and remaining universe constitutes the surroundings. The surroundings include everything other than the system. System and the surroundings together constitute the universe. The universe = The system + The surroundings However, the entire universe other than the system is not affected by the changes taking place in the system. Therefore, for all practical purposes, the surroundings are that portion of the remaining universe which can interact with the system. Usually, the region of space in the neighbourhood of the system constitutes its surroundings. For example, if we are studying the reaction between two substances A and B kept in a beaker, the beaker containing the reaction mixture is the system and the room where the beaker is kept is the surroundings (Fig. 5.1). Fig. 5.1 System and the surroundings the system from the surroundings is called boundary. This is designed to allow us to control and keep track of all movements of matter and energy in or out of the system. 5.1.2 Types of the System We, further classify the systems according to the movements of matter and energy in or out of the system. 1. Open System In an open system, there is exchange of energy and matter between system and surroundings [Fig. 5.2 (a)]. The presence of reactants in an open beaker is an example of an open system*. Here the boundary is an imaginary surface enclosing the beaker and reactants. 2. Closed System In a closed system, there is no exchange of matter, but exchange of energy is possible between system and the surroundings [Fig. 5.2 (b)]. The presence of reactants in a closed vessel made of conducting material e.g., copper or steel is an example of a closed system. Fig. 5.2 Open, closed and isolated systems. Note that the system may be defined by physical boundaries, like beaker or test tube, or the system may simply be defined by a set of Cartesian coordinates specifying a particular volume in space. It is necessary to think of the system as separated from the surroundings by some sort of wall which may be real or imaginary. The wall that separates * We could have chosen only the reactants as system then walls of the beakers will act as boundary. Rationalised 2023-24 138 chemIstry 3. Isolated System In an isolated system, there is no exchange of energy or matter between the system and the surroundings [Fig. 5.2 (c)]. The presence of reactants in a thermos flask or any other closed insulated vessel is an example of an isolated system. 5.1.3 The State of the System The system must be described in order to make any useful calculations by specifying quantitatively each of the properties such as its pressure (p), volume (V), and temperature (T ) as well as the composition of the system. We need to describe the system by specifying it before and after the change. You would recall from your Physics course that the state of a system in mechanics is completely specified at a given instant of time, by the position and velocity of each mass point of the system. In thermodynamics, a different and much simpler concept of the state of a system is introduced. It does not need detailed knowledge of motion of each particle because, we deal with average measurable properties of the system. We specify the state of the system by state

functions or state variables. The state of a thermodynamic system is described by its measurable or macroscopic (bulk) properties. We can describe the state of a gas by quoting its pressure (p), volume (V), temperature (T ), amount (n) etc. Variables like p, V, T are called state variables or state functions because their values depend only on the state of the system and not on how it is reached. In order to completely define the state of a system it is not necessary to define all the properties of the system; as only a certain number of properties can be varied independently. This number depends on the nature of the system. Once these minimum number of macroscopic properties are fixed, others automatically have definite values. The state of the surroundings can never be completely specified; fortunately it is not necessary to do so. 5.1.4 The Internal Energy as a State Function When we talk about our chemical system losing or gaining energy, we need to introduce a quantity which represents the total energy of the system. It may be chemical, electrical, mechanical or any other type of energy you may think of, the sum of all these is the energy of the system. In thermodynamics, we call it the internal energy, U of the system, which may change, when • heat passes into or out of the system, • work is done on or by the system, • matter enters or leaves the system. These systems are classified accordingly as you have already studied in section 5.1.2. (a) Work Let us first examine a change in internal energy by doing work. We take a system containing some quantity of water in a thermos flask or in an insulated beaker. This would not allow exchange of heat between the system and surroundings through its boundary and we call this type of system as adiabatic. The manner in which the state of such a system may be changed will be called adiabatic process. Adiabatic process is a process in which there is no transfer of heat between the system and surroundings. Here, the wall separating the system and the surroundings is called the adiabatic wall (Fig. 5.3). Fig. 5.3 An adiabatic system which does not permit the transfer of heat through its boundary. Let us bring the change in the internal energy of the system by doing some work on it. Let us call the initial state of the system as state A and its temperature as $T_A$. Let the internal energy of the system in state A be called $U_A$. We can change the state of the system in two different ways. Rationalised 2023-24 THERMODYNAMICS 139 One way: We do some mechanical work, say 1 kJ, by rotating a set of small paddles and thereby churning water. Let the new state be called B state and its temperature, as $T_B$. It is found that $T_B > T_A$ and the change in temperature, $\Delta T = T_B - T_A$. Let the internal energy of the system in state B be $U_B$ and the change in internal energy, $\Delta U = U_B - U_A$. Second way: We now do an equal amount (i.e., 1kJ) electrical work with the help of an immersion rod and note down the temperature change. We find that the change in temperature is same as in the earlier case, say, $T_B - T_A$. In fact, the experiments in the above manner were done by J. P. Joule between 1840–50 and he was able to show that a given amount of work done on the system, no matter how it was done (irrespective of path) produced the same change of state, as measured by the change in the temperature of the system. So, it seems appropriate to define a quantity, the internal energy U, whose value is characteristic of the state of a system, whereby the adiabatic work, $w_{ad}$ required to bring about a change of state is equal to the difference between the value of U in one state and that in another state, $\Delta U$ i.e., $\Delta U = U_2 - U_1 = w_{ad}$ Therefore, internal energy, U, of the system is a state function. By conventions of IUPAC in chemical thermodynamics. The positive sign expresses that $w_{ad}$ is positive when work is done on the system and the internal energy of system increases. Similarly, if the work is done by the system, $w_{ad}$ will be negative because internal energy of the system decreases. Can you name some other familiar state functions? Some of other familiar state functions are V, p, and T. For example, if we bring a change in temperature of the system from 25°C to 35°C, the change in temperature is 35°C–25°C = +10°C, whether we go straight up to 35°C or we cool the system for a few degrees, then take the system to the final temperature. Thus, T is a state function and the change in temperature is independent of the route taken. Volume of water in a pond, for example, is a state function, because change in volume of its water is independent of the route by which water is filled in the pond, either by rain or by tubewell or by both. (b) Heat We can also

change the internal energy of a system by transfer of heat from the surroundings to the system or vice-versa without expenditure of work. This exchange of energy, which is a result of temperature difference is called heat, q. Let us consider bringing about the same change in temperature (the same initial and final states as before in section 5.1.4 (a) by transfer of heat through thermally conducting walls instead of adiabatic walls (Fig. 5.4). We take water at temperature, TA in a container having thermally conducting walls, say made up of copper and enclose it in a huge heat reservoir at temperature, TB. The heat absorbed by the system (water), q can be measured in terms of temperature difference, TB – TA. In this case change in internal energy, ΔU = q, when no work is done at constant volume. By conventions of IUPAC in chemical thermodynamics. The q is positive, when heat is transferred from the surroundings to the system and the internal energy of the system increases and q is negative when heat is transferred from system to the surroundings resulting in decrease of the internal energy of the system. * Earlier negative sign was assigned when the work is done on the system and positive sign when the work is done by the system. This is still followed in physics books, although IUPAC has recommended the use of new sign convention. Fig. 5.4 A system which allows heat transfer through its boundary. Rationalised 2023-24 140 chemIstry (c) The general case Let us consider the general case in which a change of state is brought about both by doing work and by transfer of heat. We write change in internal energy for this case as: ΔU = q + w (5.1) For a given change in state, q and w can vary depending on how the change is carried out. However, q +w = ΔU will depend only on initial and final state. It will be independent of the way the change is carried out. If there is no transfer of energy as heat or as work (isolated system) i.e., if w = 0 and q = 0, then Δ U = 0. The equation 5.1 i.e., ΔU = q + w is mathematical statement of the first law of thermodynamics, which states that The energy of an isolated system is constant. It is commonly stated as the law of conservation of energy i.e., energy can neither be created nor be destroyed. Note: There is considerable difference between the character of the thermodynamic property energy and that of a mechanical property such as volume. We can specify an unambiguous (absolute) value for volume of a system in a particular state, but not the absolute value of the internal energy. However, we can measure only the changes in the internal energy, ΔU of the system. Problem 5.1 Express the change in internal energy of a system when (i) No heat is absorbed by the system from the surroundings, but work (w) is done on the system. What type of wall does the system have ? (ii) No work is done on the system, but q amount of heat is taken out from the system and given to the surroundings. What type of wall does the system have? (iii) w amount of work is done by the system and q amount of heat is supplied to the system. What type of system would it be? Solution (i) Δ U = w ad, wall is adiabatic (ii) Δ U = – q, thermally conducting walls (iii) Δ U = q – w, closed system. 5.2 Applications Many chemical reactions involve the generation of gases capable of doing mechanical work or the generation of heat. It is important for us to quantify these changes and relate them to the changes in the internal energy. Let us see how! 5.2.1 Work First of all, let us concentrate on the nature of work a system can do. We will consider only mechanical work i.e., pressure-volume work. For understanding pressure-volume work, let us consider a cylinder which contains one mole of an ideal gas fitted with a frictionless piston. Total volume of the gas is Vi and pressure of the gas inside is p. If external pressure is pex which is greater than p, piston is moved inward till the pressure Fig. 5.5 (a)Work done on an ideal gas in a cylinder when it is compressed by a constant external pressure, pex (in single step) is equal to the shaded area. Rationalised 2023-24 THERMODYNAMICS 141 inside becomes equal to pex. Let this change be achieved in a single step and the final volume be Vf . During this compression, suppose piston moves a distance, l and is cross-sectional area of the piston is A [Fig. 5.5(a)]. then, volume change = l × A = ΔV = (Vf – Vi ) We also know, pressure = Therefore, force on the piston = pex . A If w is the work done on the system by movement of the piston then w = force × distance = pex . A .l = pex . (–ΔV) = – pex ΔV = – pex (Vf – Vi ) (5.2) The negative sign of this expression is required to obtain conventional sign for w, which will be positive. It indicates that in

case of compression work is done on the system. Here ($V_f - V_i$) will be negative and negative multiplied by negative will be positive. Hence the sign obtained for the work will be positive. If the pressure is not constant at every stage of compression, but changes in number of finite steps, work done on the gas will be summed over all the steps and will be equal to $-\Sigma p\,\Delta V$ [Fig. 5.5 (b)] If the pressure is not constant but changes during the process such that it is always infinitesimally greater than the pressure of the gas, then, at each stage of compression, the volume decreases by an infinitesimal amount, dV. In such a case we can calculate the work done on the gas by the relation

$$w = -\int_{V_i}^{V_f} p_{ex}\,dV \quad (5.3)$$

Here, $p_{ex}$ at each stage is equal to ($p_{in}$ + dp) in case of compression [Fig. 5.5(c)]. In an expansion process under similar conditions, the external pressure is always less than the pressure of the system i.e., $p_{ex}$ = ($p_{in}$– dp). In general case we can write, $p_{ex}$ = ($p_{in}$ + dp). Such processes are called reversible processes. A process or change is said to be reversible, if a change is brought out in such a way that the process could, at any moment, be reversed by an infinitesimal change. A reversible process proceeds infinitely slowly by a series of equilibrium states such that system and the surroundings are always in near equilibrium with each other. Fig.5.5 (c) pV-plot when pressure is not constant and changes in infinite steps (reversible conditions) during compression from initial volume, $V_i$ to final volume, $V_f$. Work done on the gas is represented by the shaded area. Fig.5.5 (b) pV-plot when pressure is not constant and changes in finite steps during compression from initial volume, $V_i$ to final volume, $V_f$. Work done on the gas is represented by the shaded area.

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Processes other than reversible processes are known as irreversible processes. In chemistry, we face problems that can be solved if we relate the work term to the internal pressure of the system. We can relate work to internal pressure of the system under reversible conditions by writing equation 5.3 as follows:

$$w_{rev} = -\int_{V_i}^{V_f} p_{ex}\,dV = -\int_{V_i}^{V_f} (p_{in} \pm dp)\,dV$$

Since dp × dV is very small we can write

$$w_{rev} = -\int_{V_i}^{V_f} p\,dV \quad (5.4)$$

Now, the pressure of the gas ($p_{in}$ which we can write as p now) can be expressed in terms of its volume through gas equation. For n mol of an ideal gas i.e., pV =nRT

$$\Rightarrow p = \frac{nRT}{V}$$

Therefore, at constant temperature (isothermal process),

$$w_{rev} = -\int_{V_i}^{V_f} nRT \frac{dV}{V} = -nRT \ln\frac{V_f}{V_i} = -2.303\, nRT \log\frac{V_f}{V_i} \quad (5.5)$$

Free expansion: Expansion of a gas in vacuum ($p_{ex}$ = 0) is called free expansion. No work is done during free expansion of an ideal gas whether the process is reversible or irreversible (equation 5.2 and 5.3).

Now, we can write equation 5.1 in number of ways depending on the type of processes. Let us substitute w = − $p_{ex}\Delta V$ (eq. 5.2) in equation 5.1, and we get

$$\Delta U = q - p_{ex}\Delta V$$

If a process is carried out at constant volume ($\Delta V$ = 0), then $\Delta U = q_V$ the subscript V in $q_V$ denotes that heat is supplied at constant volume. Isothermal and free expansion of an ideal gas For isothermal (T = constant) expansion of an ideal gas into vacuum; w = 0 since $p_{ex}$ = 0. Also, Joule determined experimentally that q = 0; therefore, $\Delta U$ = 0 Equation 5.1, can be expressed for isothermal irreversible and reversible changes as follows:

1. For isothermal irreversible change q = − w = $p_{ex}$ ($V_f - V_i$)
2. For isothermal reversible change q = − w = nRT ln = 2.303 nRT log $\frac{V_f}{V_i}$ For adiabatic change, q = 0, $\Delta U$ = $w_{ad}$

Problem 5.2 Two litres of an ideal gas at a pressure of 10 atm expands isothermally at 25 °C into a vacuum until its total volume is 10 litres. How much heat is absorbed and how much work is done in the expansion ? Solution We have q = − w = $p_{ex}$ (10 − 2) = 0(8) = 0 No work is done; no heat is absorbed. Problem 5.3 Consider the same expansion, but this time against a constant external pressure of 1 atm. Solution We have q = − w = $p_{ex}$ (8) = 8 litre-atm Problem 5.4 Consider the expansion given in problem 5.2, for 1 mol of an ideal gas conducted reversibly. Solution We have q = − w = 2.303 nRT log $\frac{V_f}{V_s}$ = 2.303 × 1 × 0.8206 × 298 × log $\frac{10}{2}$

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Remember $\Delta H = q_p$, heat absorbed by the system at constant pressure. $\Delta H$ is negative for exothermic reactions which evolve heat during the reaction and $\Delta H$ is positive for endothermic reactions which absorb heat from the surroundings. At constant volume ($\Delta V$ = 0), $\Delta U = q_V$, therefore equation 5.8 becomes $\Delta H = \Delta U = q_V$ The difference between $\Delta H$ and $\Delta U$ is not usually significant for systems consisting of only solids and / or liquids. Solids and liquids do not suffer any

significant volume changes upon heating. The difference, however, becomes significant when gases are involved. Let us consider a reaction involving gases. If $V_A$ is the total volume of the gaseous reactants, $V_B$ is the total volume of the gaseous products, $n_A$ is the number of moles of gaseous reactants and $n_B$ is the number of moles of gaseous products, all at constant pressure and temperature, then using the ideal gas law, we write, $pV_A = n_ART$ and $pV_B = n_BRT$ Thus, $pV_B - pV_A = n_BRT - n_ART = (n_B-n_A)RT$ or $p(V_B - V_A) = (n_B - n_A) RT$ or $p \Delta V = \Delta n_g RT$ (5.9) Here, $\Delta n_g$ refers to the number of moles of gaseous products minus the number of moles of gaseous reactants. Substituting the value of $p\Delta V$ from equation 5.9 in equation 5.8, we get $\Delta H = \Delta U + \Delta n_g RT$ (5.10) The equation 5.10 is useful for calculating $\Delta H$ from $\Delta U$ and vice versa. Problem 5.5 If water vapour is assumed to be a perfect gas, molar enthalpy change for vapourisation of 1 mol of water at 1bar and 100°C is 41kJ mol–1. Calculate the internal energy change, when = 2.303 x 0.8206 x 298 x log 5 = 2.303 x 0.8206 x 298 x 0.6990 = 393.66 L atm 5.2.2 Enthalpy, H (a) A Useful New State Function We know that the heat absorbed at constant volume is equal to change in the internal energy i.e., $\Delta U = q_V$. But most of chemical reactions are carried out not at constant volume, but in flasks or test tubes under constant atmospheric pressure. We need to define another state function which may be suitable under these conditions. We may write equation (5.1) as $\Delta U = q_p - p\Delta V$ at constant pressure, where $q_p$ is heat absorbed by the system and $-p\Delta V$ represent expansion work done by the system. Let us represent the initial state by subscript 1 and final state by 2 We can rewrite the above equation as $U_2-U_1 = q_p - p(V_2 - V_1)$ On rearranging, we get $q_p = (U_2 + pV_2) - (U_1 + pV_1)$ (5.6) Now we can define another thermodynamic function, the enthalpy H [Greek word enthalpien, to warm or heat content] as : $H = U + pV$ (5.7) so, equation (5.6) becomes $q_p = H_2 - H_1 = \Delta H$ Although q is a path dependent function, H is a state function because it depends on U, p and V, all of which are state functions. Therefore, $\Delta H$ is independent of path. Hence, $q_p$ is also independent of path. For finite changes at constant pressure, we can write equation 5.7 as $\Delta H = \Delta U + \Delta pV$ Since p is constant, we can write $\Delta H = \Delta U + p\Delta V$ (5.8) It is important to note that when heat is absorbed by the system at constant pressure, we are actually measuring changes in the enthalpy. Rationalised 2023-24 144 chemIstry 1 mol of water is vapourised at 1 bar pressure and 100°C. Solution (i) The change $H_2O (l) \rightarrow H_2O (g)$ $\Delta H = \Delta U + \Delta n_g RT$ or $\Delta U = \Delta H - \Delta n_g RT$, substituting the values, we get $\Delta U = 41.00$ kJ mol–1 $- 1 \times 8.3$ J mol–1 K–1 $\times 373$ K $= 41.00$ kJ mol-1 $- 3.096$ kJ mol-1 $= 37.904$ kJ mol–1 (c) Heat Capacity In this sub-section, let us see how to measure heat transferred to a system. This heat appears as a rise in temperature of the system in case of heat absorbed by the system. The increase of temperature is proportional to the heat transferred $q$ $c$ - oeff $T$ The magnitude of the coefficient depends on the size, composition and nature of the system. We can also write it as $q = C \Delta T$ The coefficient, C is called the heat capacity. Thus, we can measure the heat supplied by monitoring the temperature rise, provided we know the heat capacity. When C is large, a given amount of heat results in only a small temperature rise. Water has a large heat capacity i.e., a lot of energy is needed to raise its temperature. C is directly proportional to amount of substance. The molar heat capacity of a substance, $C_m = C$ $n$ - , is the heat capacity for one mole of the substance and is the quantity of heat needed to raise the temperature of one mole by one degree celsius (or one kelvin). Specific heat, also called specific heat capacity is the quantity Fig. 5.6(a) A gas at volume V and temperature T Fig. 5.6 (b) Partition, each part having half the volume of the gas (b) Extensive and Intensive Properties In thermodynamics, a distinction is made between extensive properties and intensive properties. An extensive property is a property whose value depends on the quantity or size of matter present in the system. For example, mass, volume, internal energy, enthalpy, heat capacity, etc. are extensive properties. Those properties which do not depend on the quantity or size of matter present are known as intensive properties. For example temperature, density, pressure etc. are intensive properties. A molar property, $\chi_m$, is the value of an extensive property $\chi$ of the system for 1 mol of the substance. If n is the amount of matter, $m$ - $n$ is independent of the amount of matter. Other examples are molar

volume, Vm and molar heat capacity, Cm. Let us understand the distinction between extensive and intensive properties by considering a gas enclosed in a container of volume V and at temperature T [Fig. 5.6(a)]. Let us make a partition such that volume is halved, each part [Fig. 5.6 (b)] now has one half of the original volume, V 2 , but the temperature will still remain the same i.e., T. It is clear that volume is an extensive property and temperature is an intensive property. Rationalised 2023-24 THERMODYNAMICS 145 of heat required to raise the temperature of one unit mass of a substance by one degree celsius (or one kelvin). For finding out the heat, q, required to raise the temperatures of a sample, we multiply the specific heat of the substance, c, by the mass m, and temperatures change, ΔT as q c  - m T -  ⬚ ⬚ C T (5.11) (d) The Relationship between Cp and CV for an Ideal Gas At constant volume, the heat capacity, C is denoted by CV and at constant pressure, this is denoted by Cp . Let us find the relationship between the two. We can write equation for heat, q at constant volume as qV = C T V   - U at constant pressure as qp = C T p  - H The difference between Cp and CV can be derived for an ideal gas as: For a mole of an ideal gas, ΔH = ΔU + Δ(pV ) = ΔU + Δ(RT ) = ΔU + RΔT  - ⬚ ⬚ H U ⬚ R ⬚T (5.12) On putting the values of ΔH and ΔU, we have C T p V   -  ⬚ C T RT C C p V  - R Cp – CV = R (5.13) 5.3 Measurement of ΔU and ΔH: Calorimetry We can measure energy changes associated with chemical or physical processes by an experimental technique called calorimetry. In calorimetry, the process is carried out in a vessel called calorimeter, which is immersed in a known volume of a liquid. Knowing the heat capacity of the liquid in which calorimeter is immersed and the heat capacity of calorimeter, it is possible to determine the heat evolved in the process by measuring temperature changes. Measurements are made under two different conditions: i) at constant volume, qV ii) at constant pressure, qp (a) ΔU Measurements For chemical reactions, heat absorbed at constant volume, is measured in a bomb calorimeter (Fig. 5.7). Here, a steel vessel (the bomb) is immersed in a water bath. The whole device is called calorimeter. The steel vessel is immersed in water bath to ensure that no heat is lost to the surroundings. A combustible Fig. 5.7 Bomb calorimeter substance is burnt in pure dioxygen supplied in the steel bomb. Heat evolved during the reaction is transferred to the water around the bomb and its temperature is monitored. Since the bomb calorimeter is sealed, its volume does not change i.e., the energy changes associated with reactions are measured at constant volume. Under these conditions, no work is done as the reaction is carried out at constant volume in the bomb calorimeter. Even for reactions involving gases, there is no work done as ΔV = 0. Temperature change of the calorimeter produced by the completed reaction is then converted to qV, by using the known heat capacity of the calorimeter with the help of equation 5.11. Rationalised 2023-24 146 chemIstry (b) ΔH Measurements Measurement of heat change at constant pressure (generally under atmospheric pressure) can be done in a calorimeter shown in Fig. 5.8. We know that ΔH = qp (at constant p) and, therefore, heat absorbed or evolved, qp at constant pressure is also called the heat of reaction or enthalpy of reaction, Δr H. In an exothermic reaction, heat is evolved, and system loses heat to the surroundings. Therefore, qp will be negative and Δr H will also be negative. Similarly in an endothermic reaction, heat is absorbed, qp is positive and Δr H will be positive. Problem 5.6 1g of graphite is burnt in a bomb calorimeter in excess of oxygen at 298 K and 1 atmospheric pressure according to the equation C (graphite) + O2 (g) → CO2 (g) During the reaction, temperature rises from 298 K to 299 K. If the heat capacity Fig. 5.8 Calorimeter for measuring heat changes at constant pressure (atmospheric pressure). of the bomb calorimeter is 20.7kJ/K, what is the enthalpy change for the above reaction at 298 K and 1 atm? Solution Suppose q is the quantity of heat from the reaction mixture and CV is the heat capacity of the calorimeter, then the quantity of heat absorbed by the calorimeter. q = CV × ΔT Quantity of heat from the reaction will have the same magnitude but opposite sign because the heat lost by the system (reaction mixture) is equal to the heat gained by the calorimeter. q = –CV × ΔT = – 20.7 kJ/K × (299 – 298) K = – 20.7 kJ (Here, negative sign indicates the exothermic nature of the reaction) Thus, ΔU for the combustion of the 1g of graphite = – 20.7 kJK–1 For combustion of 1 mol of graphite, = 12 0 2 mol 0 7 1 1 . . g kJ g  - ⬚ ⬚ = −

$2.48 \times 10^2$ kJ mol$^{-1}$, Since $\Delta n_g = 0$, $\Delta H = \Delta U = -2.48 \times 10^2$ kJ mol$^{-1}$

## 5.4 Enthalpy change, $\Delta_r H$ of a reaction – Reaction Enthalpy

In a chemical reaction, reactants are converted into products and is represented by,

Reactants → Products

The enthalpy change accompanying a reaction is called the reaction enthalpy. The enthalpy change of a chemical reaction, is given by the symbol $\Delta_r H$

$\Delta_r H$ = (sum of enthalpies of products) – (sum of enthalpies of reactants)

$$= \sum_i a_i H_{products} - \sum_i b_i H_{reactants} \quad (5.14)$$

Here symbol $\sum$ (sigma) is used for summation and $a_i$ and $b_i$ are the stoichiometric

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coefficients of the products and reactants respectively in the balanced chemical equation. For example, for the reaction

CH$_4$ (g) + 2O$_2$ (g) → CO$_2$ (g) + 2H$_2$O (l)

$$\Delta_r H = \sum_i a_i H_{Products} - \sum_i b_i H_{reactants}$$

$= [H_m (CO_2, g) + 2H_m (H_2O, l)] - [H_m (CH_4, g) + 2H_m (O_2, g)]$

where $H_m$ is the molar enthalpy.

Enthalpy change is a very useful quantity. Knowledge of this quantity is required when one needs to plan the heating or cooling required to maintain an industrial chemical reaction at constant temperature. It is also required to calculate temperature dependence of equilibrium constant.

**(a) Standard Enthalpy of Reactions**

Enthalpy of a reaction depends on the conditions under which a reaction is carried out. It is, therefore, necessary that we must specify some standard conditions. The standard enthalpy of reaction is the enthalpy change for a reaction when all the participating substances are in their standard states.

The standard state of a substance at a specified temperature is its pure form at 1 bar. For example, the standard state of liquid ethanol at 298 K is pure liquid ethanol at 1 bar; standard state of solid iron at 500 K is pure iron at 1 bar. Usually data are taken at 298 K.

Standard conditions are denoted by adding the superscript 0 to the symbol $\Delta H$, e.g., $\Delta H^0$

**(b) Enthalpy Changes during Phase Transformations**

Phase transformations also involve energy changes. Ice, for example, requires heat for melting. Normally this melting takes place at constant pressure (atmospheric pressure) and during phase change, temperature remains constant (at 273 K).

H$_2$O(s) → H$_2$O(l); $\Delta_{fus}H^0$ = 6.00 kJ mol$^{-1}$

Here $\Delta_{fus}H^0$ is enthalpy of fusion in standard state. If water freezes, then process is reversed and equal amount of heat is given off to the surroundings.

The enthalpy change that accompanies melting of one mole of a solid substance in standard state is called standard enthalpy of fusion or molar enthalpy of fusion, $\Delta_{fus}H^0$.

Melting of a solid is endothermic, so all enthalpies of fusion are positive. Water requires heat for evaporation. At constant temperature of its boiling point $T_b$ and at constant pressure:

**Table 5.1 Standard Enthalpy Changes of Fusion and Vaporisation** ($T_f$ and $T_b$ are melting and boiling points, respectively)

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H$_2$O(l) → H$_2$O(g); $\Delta_{vap}H^0$ = + 40.79 kJ mol$^{-1}$

$\Delta_{vap}H^0$ is the standard enthalpy of vaporisation.

Amount of heat required to vaporize one mole of a liquid at constant temperature and under standard pressure (1bar) is called its standard enthalpy of vaporization or molar enthalpy of vaporization, $\Delta_{vap}H^0$.

Sublimation is direct conversion of a solid into its vapour. Solid CO$_2$ or 'dry ice' sublimes at 195K with $\Delta_{sub}H^0$=25.2 kJ mol$^{-1}$; naphthalene sublimes slowly and for this $\Delta_{sub}H^0$ = 73.0 kJ mol$^{-1}$.

Standard enthalpy of sublimation, $\Delta_{sub}H^0$ is the change in enthalpy when one mole of a solid substance sublimes at a constant temperature and under standard pressure (1bar).

The magnitude of the enthalpy change depends on the strength of the intermolecular interactions in the substance undergoing the phase transfomations. For example, the strong hydrogen bonds between water molecules hold them tightly in liquid phase. For an organic liquid, such as acetone, the intermolecular dipole-dipole interactions are significantly weaker. Thus, it requires less heat to vaporise 1 mol of acetone than it does to vaporize 1 mol of water. Table 5.1 gives values of standard enthalpy changes of fusion and vaporisation for some substances.

**Solution**

We can represent the process of evaporation as

vaporisation
H$_2$O(l) $\xrightarrow{\hspace{1.5cm}}$ H$_2$O(g)
1mol      1mol

No. of moles in 18 g H$_2$O(l) is

$= \dfrac{18g}{18g\ mol^{-1}} = 1$ mol

Heat supplied to evaporate18g water at 298 K = n × $\Delta_{vap}H^0$

= (1 mol) × (44.01 kJ mol$^{-1}$)

= 44.01 kJ

(assuming steam behaving as an ideal gas).

$\Delta_{vap}U = \Delta_{vap}H^0 - p\Delta V = \Delta_{vap}H^0 - \Delta n_g RT$

$\Delta_{vap}H^V - \Delta n_g RT$ = 44.01 kJ $-(1)(8.314$ JK$^{-1}$mol$^{-1})(298K)(10^{-3}$kJ J$^{-1})$

$\Delta_{vap}U^V$ = 44.01 kJ $-$ 2.48kJ

= 41.53 kJ

Problem 5.8 Assuming the water vapour

to be a perfect gas, calculate the internal energy change when 1 mol of water at 100°C and 1 bar pressure is converted to ice at 0°C. Given the enthalpy of fusion of ice is 6.00 kJ mol-1 heat capacity of water is 4.2 J/g°C The change take place as follows: Step - 1 1 mol H2O (l, 100°C) ◊ 1 mol (l, 0°C) Enthalpy change ΔH1 Step - 2 1 mol H2O (l, 0°C) ◊ 1 mol H2O( S, 0°C) Enthalpy change ΔH2 Total enthalpy change will be - ΔH = ΔH1 + ΔH2 ΔH1 = - (18 x 4.2 x 100) J mol-1 = - 7560 J mol-1 = - 7.56 k J mol-1 ΔH2 = - 6.00 kJ mol-1 Problem 5.7 A swimmer coming out from a pool is covered with a film of water weighing about 18g. How much heat must be supplied to evaporate this water at 298 K ? Calculate the internal energy of vaporisation at 298K. Δvap H0 for water at 298K= 44.01kJ mol–1 Rationalised 2023-24 THERMODYNAMICS 149 of aggregation (also known as reference states) is called Standard Molar Enthalpy of Formation. Its symbol is Δf H0, where the subscript ' f ' indicates that one mole of the compound in question has been formed in its standard state from its elements in their most stable states of aggregation. The reference state of an element is its most stable state of aggregation at 25°C and 1 bar pressure. For example, the reference state of dihydrogen is H2 gas and those of dioxygen, carbon and sulphur are O2 gas, Cgraphite and Srhombic respectively. Some reactions with standard molar enthalpies of formation are as follows. Table 5.2 Standard Molar Enthalpies of Formation (Δf H ψ) at 298K of a Few Selected Substances Therefore, ΔH = - 7.56 kJ mol-1 + (-6.00 kJ mol-1) = -13.56 kJ mol-1 There is negligible change in the volume during the change form liquid to solid state. Therefore, pΔv = Δng RT = 0 ΔH = ΔU = - 13.56kJ mol-1 (c) Standard Enthalpy of Formation The standard enthalpy change for the formation of one mole of a compound from its elements in their most stable states Rationalised 2023-24 150 chemIstry H2(g) + ½O2 (g) → H2O(1); Δf H0 = –285.8 kJ mol–1 C (graphite, s) + 2H2(g) → Ch4 (g); Δf H0 = –74.81 kJ mol–1 2C (graphite, s)+3H2 (g)+ ½O2(g) → C2H5OH(1); Δf H0 = – 277.7kJ mol–1 It is important to understand that a standard molar enthalpy of formation, Δf H 0, is just a special case of Δr H0, where one mole of a compound is formed from its constituent elements, as in the above three equations, where 1 mol of each, water, methane and ethanol is formed. In contrast, the enthalpy change for an exothermic reaction: CaO(s) + CO2(g) → CaCo3(s); Δr H0 = – 178.3kJ mol–1 is not an enthalpy of formation of calcium carbonate, since calcium carbonate has been formed from other compounds, and not from its constituent elements. Also, for the reaction given below, enthalpy change is not standard enthalpy of formation, Δf H0 for HBr(g). H2(g) + Br2(l) → 2HBr(g); Δr H0 = – 178.3kJ mol–1 Here two moles, instead of one mole of the product is formed from the elements, i.e., Δr H0 = 2Δf H0 Therefore, by dividing all coefficients in the balanced equation by 2, expression for enthalpy of formation of HBr (g) is written as ½H2(g) + ½Br2(1) → HBr(g); Δf H0 = – 36.4 kJ mol–1 Standard enthalpies of formation of some common substances are given in Table 5.2. By convention, standard enthalpy for formation, Δf H0, of an element in reference state, i.e., its most stable state of aggregation is taken as zero. Suppose, you are a chemical engineer and want to know how much heat is required to decompose calcium carbonate to lime and carbon dioxide, with all the substances in their standard state. CaCO3(s) → CaO(s) + CO2(g); Δr H0 = ? Here, we can make use of standard enthalpy of formation and calculate the enthalpy change for the reaction. The following general equation can be used for the enthalpy change calculation. Δr H0 = i ∑ ai Δf H0 (products) – i ∑ bi Δf H0 (reactants) (5.15) where a and b represent the coefficients of the products and reactants in the balanced equation. Let us apply the above equation for decomposition of calcium carbonate. Here, coefficients 'a' and 'b' are 1 each. Therefore, Δr H0 = Δf H0 = [CaO(s)]+ Δf H0 [CO2(g)] – Δf H0 = [CaCO3(s)] =1 (–635.1 kJ mol–1) + 1(–393.5 kJ mol–1) –1(–1206.9 kJ mol–1) = 178.3 kJ mol–1 Thus, the decomposition of CaCO3 (s) is an endothermic process and you have to heat it for getting the desired products. (d) Thermochemical Equations A balanced chemical equation together with the value of its Δr H is called a thermochemical equation. We specify the physical state (alongwith allotropic state) of the substance in an equation. For example: C2H5OH(l) + 3O2(g) → 2CO2(g) + 3H2O(l); Δr H0 = – 1367 kJ mol–1 The

above equation describes the combustion of liquid ethanol at constant temperature and pressure. The negative sign of enthalpy change indicates that this is an exothermic reaction. It would be necessary to remember the following conventions regarding thermochemical equations. 1. The coefficients in a balanced thermochemical equation refer to the number of moles (never molecules) of reactants and products involved in the reaction. 2. The numerical value of $\Delta_r H^0$ refers to the number of moles of substances specified by an equation. Standard enthalpy change $\Delta_r H^0$ will have units as kJ mol$^{-1}$.

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To illustrate the concept, let us consider the calculation of heat of reaction for the following reaction :

$Fe_2O_3(s) + 3H_2(g) \rightarrow 2Fe(s) + 3H_2O(l)$,

From the Table (5.2) of standard enthalpy of formation ($\Delta_f H^0$), we find :

$\Delta_f H^0$ (H2O,l) = –285.83 kJ mol$^{-1}$; $\Delta_f H^0$ (Fe2O3,s) = – 824.2 kJ mol$^{-1}$; Also $\Delta_f H^0$ (Fe, s) = 0 and $\Delta_f H^0$ (H2, g) = 0 as per convention

Then, $\Delta_f H_1^0$ = 3(–285.83 kJ mol$^{-1}$) – 1(– 824.2 kJ mol$^{-1}$) = (–857.5 + 824.2) kJ mol$^{-1}$ = –33.3 kJ mol$^{-1}$

Note that the coefficients used in these calculations are pure numbers, which are equal to the respective stoichiometric coefficients. The unit for $\Delta_r H^0$ is kJ mol$^{-1}$, which means per mole of reaction. Once we balance the chemical equation in a particular way, as above, this defines the mole of reaction. If we had balanced the equation differently, for example,

$\frac{1}{2} Fe_2O_3(s) + \frac{3}{2} H_2(g) \rightarrow Fe(s) + \frac{3}{2} H_2O(l)$

then this amount of reaction would be one mole of reaction and $\Delta_r H^0$ would be

$\Delta_f H_2^0 = \frac{3}{2}$ (–285.83 kJ mol$^{-1}$) – $\frac{1}{2}$ (–824.2 kJ mol$^{-1}$) = (– 428.7 + 412.1) kJ mol$^{-1}$ = – 16.6 kJ mol$^{-1}$ = ½ $\Delta_r H_1^0$

It shows that enthalpy is an extensive quantity.

3. When a chemical equation is reversed, the value of $\Delta_r H^0$ is reversed in sign. For example

$N_2(g) + 3H_2 (g) \rightarrow 2NH_3 (g)$; $\Delta_r H^0$ = – 91.8 kJ. mol$^{-1}$

$2NH_3(g) \rightarrow N_2(g) + 3H_2 (g)$; $\Delta_r H^0$ = + 91.8 kJ mol$^{-1}$

(e) Hess's Law of Constant Heat Summation

We know that enthalpy is a state function, therefore the change in enthalpy is independent of the path between initial state (reactants) and final state (products). In other words, enthalpy change for a reaction is the same whether it occurs in one step or in a series of steps. This may be stated as follows in the form of Hess's Law. If a reaction takes place in several steps then its standard reaction enthalpy is the sum of the standard enthalpies of the intermediate reactions into which the overall reaction may be divided at the same temperature.

Let us understand the importance of this law with the help of an example.

Consider the enthalpy change for the reaction

C (graphite,s) + O2 (g) $\rightarrow$ CO (g); $\Delta_r H^0$ = ?

Although CO(g) is the major product, some CO2 gas is always produced in this reaction. Therefore, we cannot measure enthalpy change for the above reaction directly. However, if we can find some other reactions involving related species, it is possible to calculate the enthalpy change for the above reaction.

Let us consider the following reactions:

C (graphite,s) + O2 (g) $\rightarrow$ CO2 (g); $\Delta_r H^0$ = – 393.5 kJ mol$^{-1}$ (i)

CO (g) + $\frac{1}{2}$ O2 (g) $\rightarrow$ CO2 (g) $\Delta_r H^0$ = – 283.0 kJ mol$^{-1}$ (ii)

We can combine the above two reactions in such a way so as to obtain the desired reaction. To get one mole of CO(g) on the right, we reverse equation (ii). In this, heat is absorbed instead of being released, so we change sign of $\Delta_r H^0$ value

CO2 (g) $\rightarrow$ CO (g) + O2 (g); $\Delta_r H^0$ = + 283.0 kJ mol$^{-1}$ (iii)

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Adding equation (i) and (iii), we get the desired equation,

C graphite(s); + O2(g) $\rightarrow$ CO(g) $\frac{1}{2}$ for which

$\Delta_r H^0$ = (– 393.5 + 283.0) = – 110.5 kJ mol$^{-1}$

In general, if enthalpy of an overall reaction A$\rightarrow$B along one route is $\Delta_r H$ and $\Delta_r H_1$, $\Delta_r H_2$, $\Delta_r H_3$..... representing enthalpies of reactions leading to same product, B along another route, then we have

$\Delta_r H = \Delta_r H_1 + \Delta_r H_2 + \Delta_r H_3$ ... (5.16)

It can be represented as:

5.5 Enthalpies for different types of reactions

It is convenient to give name to enthalpies specifying the types of reactions.

(a) Standard Enthalpy of Combustion (symbol : $\Delta_c H^0$)

Combustion reactions are exothermic in nature. These are important in industry, rocketry, and other walks of life. Standard enthalpy of combustion is defined as the enthalpy change per mole (or per unit amount) of a substance, when it undergoes combustion and all the reactants and products being in their standard states at the specified temperature.

Cooking gas in cylinders contains mostly butane (C4H10). During complete combustion of one mole of butane, 2658 kJ of heat is released. We can write the thermochemical reactions for

this as: C H4 10 2 g O g CO g 2 2 H O 13 2 () () () - 4 5 ( ) 1 ; $\Delta_C H^0$ = − 2658.0 kJ mol−1 Similarly, combustion of glucose gives out 2802.0 kJ/mol of heat, for which the overall equation is : C H6 12 6 O g() () () - 6 6 O g 2 2 CO g H 6 1 2O( ); $\Delta_C H^0$ = − 2802.0 kJ mol−1 Our body also generates energy from food by the same overall process as combustion, although the final products are produced after a series of complex bio-chemical reactions involving enzymes. A B C D ΔH1 Δr H2 Δr H3 Δr H **Problem 5.9** The combustion of one mole of benzene takes place at 298 K and 1 atm. After combustion, $CO_2(g)$ and $H_2O$ (1) are produced and 3267.0 kJ of heat is liberated. Calculate the standard enthalpy of formation, $\Delta_f H^0$ of benzene. Standard enthalpies of formation of $CO_2(g)$ and $H_2O(l)$ are −393.5 kJ mol−1 and − 285.83 kJ mol−1 respectively. **Solution** The formation reaction of benzene is given by : 6 3 C g 2 6 6 raphite H - ⬚ g C - ⬚ H l -; $\Delta_f H^0$ = ? ... (i) The enthalpy of combustion of 1 mol of benzene is : C H l O CO g H O l 6 6 2 2 2 15 2 - ⬚⬚ 6 3 - ⬚ -; $\Delta_C H^0$ = − 3267 kJ mol−1... (ii) The enthalpy of formation of 1 mol of $CO_2(g)$ : C g raphite O - ⬚ 2 2 g C - ⬚ O g -; $\Delta_f H^0$ = − 393.5 kJ mol−1... (iii) The enthalpy of formation of 1 mol of $H_2O(l)$ is : Hg Og H O l 2 2 2 1 2 - ⬚ - ⬚ -; $\Delta_C H^0$ = − 285.83 kJ mol−1... (iv) multiplying eqn. (iii) by 6 and eqn. (iv) by 3 we get: Rationalised 2023-24 THERMODYNAMICS 153 6 6 C g raphite O - ⬚ 2 2 g C - ⬚ 6 O g -; $\Delta_f H^0$ = − 2361 kJ mol−1 3 3 2 Hg Og 2 2 - ⬚ - ⬚ 3 1 H O2 -; $\Delta_f H^0$ = − 857.49 kJ mol−1 Summing up the above two equations : 6 3 15 2 6 3 2 2 2 2 C graphite H g O g CO g H O l - ⬚ - ⬚ - ⬚ - ⬚ -; $\Delta_f H^0$ = − 3218.49 kJ mol−1... (v) Reversing equation (ii); 6 3 15 2 CO2 2 g H O l C H6 6 2 - ⬚ - ⬚ l O - ⬚; $\Delta_f H^0$ = − 3267.0 kJ mol−1... (vi) Adding equations (v) and (vi), we get 6 3 C g 2 6 6 raphite H - ⬚ g C - ⬚ H l -; $\Delta_f H^0$ = − 48.51 kJ mol−1... (iv) In this case, the enthalpy of atomization is same as the enthalpy of sublimation. **(c) Bond Enthalpy (symbol: $\Delta_{bond}H^0$)** Chemical reactions involve the breaking and making of chemical bonds. Energy is required to break a bond and energy is released when a bond is formed. It is possible to relate heat of reaction to changes in energy associated with breaking and making of chemical bonds. With reference to the enthalpy changes associated with chemical bonds, two different terms are used in thermodynamics. (i) Bond dissociation enthalpy (ii) Mean bond enthalpy Let us discuss these terms with reference to diatomic and polyatomic molecules. **Diatomic Molecules:** Consider the following process in which the bonds in one mole of dihydrogen gas ($H_2$) are broken: $H_2(g) \rightarrow 2H(g)$; $\Delta_{H-H}H^0$ = 435.0 kJ mol−1 The enthalpy change involved in this process is the bond dissociation enthalpy of H−H bond. The bond dissociation enthalpy is the change in enthalpy when one mole of covalent bonds of a gaseous covalent compound is broken to form products in the gas phase. Note that it is the same as the enthalpy of atomization of dihydrogen. This is true for all diatomic molecules. For example: $Cl_2(g) \rightarrow 2Cl(g)$; $\Delta_{Cl-Cl}H^0$ = 242 kJ mol−1 $O_2(g) \rightarrow 2O(g)$; $\Delta_{O=O}H^0$ = 428 kJ mol−1 In the case of polyatomic molecules, bond dissociation enthalpy is different for different bonds within the same molecule. **Polyatomic Molecules:** Let us now consider a polyatomic molecule like methane, $CH_4$. The overall thermochemical equation for its atomization reaction is given below: CH (g) C(g) 4H(g); 4 → + $\Delta_a H^0$ = 1665 kJ mol−1 In methane, all the four C − H bonds are identical in bond length and energy. However, the energies required to break the individual C − H bonds in each successive step differ : **(b) Enthalpy of Atomization (symbol: $\Delta_a H^0$)** Consider the following example of atomization of dihydrogen $H_2(g) \rightarrow 2H(g)$; $\Delta_a H^0$ = 435.0 kJ mol−1 You can see that H atoms are formed by breaking H−H bonds in dihydrogen. The enthalpy change in this process is known as enthalpy of atomization, $\Delta_a H^0$. It is the enthalpy change on breaking one mole of bonds completely to obtain atoms in the gas phase. In case of diatomic molecules, like dihydrogen (given above), the enthalpy of atomization is also the bond dissociation enthalpy. The other examples of enthalpy of atomization can be $CH_4(g) \rightarrow C(g) + 4H(g)$; $\Delta_a H^0$ = 1665 kJ mol−1 Note that the products are only atoms of C and H in gaseous phase. Now see the following reaction: $Na(s) \rightarrow Na(g)$; $\Delta_a H^0$ = 108.4 kJ mol−1 Rationalised 2023-24 154 chemIstry $CH_4(g) \rightarrow CH_3(g)+H(g)$; $\Delta_{bond} H^0$ = +427 kJ mol−1 $CH_3(g) \rightarrow CH_2(g)+H(g)$; $\Delta_{bond} H^0$ = +439 kJ mol−1 $CH_2(g) \rightarrow CH(g)+H(g)$; $\Delta_{bond} H^0$ = +452 kJ mol−1 $CH(g) \rightarrow C(g)+H(g)$; $\Delta_{bond} H^0$ = +347

kJ mol–1 Therefore, CH4(g) → C(g)+4H(g);Δa H0 = 1665 kJ mol–1 In such cases we use mean bond enthalpy of C – H bond. For example in CH4, ΔC–HH0 is calculated as: ΔC–HH0 = ¼ (Δa H0) = ¼ (1665 kJ mol–1) = 416 kJ mol–1 We find that mean C–H bond enthalpy in methane is 416 kJ/mol. It has been found that mean C–H bond enthalpies differ slightly from compound to compound, as in CH3CH2Cl, CH3NO2, etc., but it does not differ in a great deal*. Using Hess's law, bond enthalpies can be calculated. Bond enthalpy values of some single and multiple bonds are given in Table 5.3. The reaction enthalpies are very important quantities as these arise from the changes that accompany the breaking of old bonds and formation of the new bonds. We can predict enthalpy of a reaction in gas phase, if we know different bond enthalpies. The standard enthalpy of reaction, Δr H0 is related to bond enthalpies of the reactants and products in gas phase reactions as: Δr H0 (5.17)** This relationship is particularly more useful when the required values of Δf H0 are not available. The net enthalpy change of a reaction is the amount of energy required to break all the bonds in the reactant molecules minus the amount of energy required to break all the bonds in the product molecules. Remember that this relationship is approximate and is valid when all substances  - ⊠ ⊠ bond enthalpies bond enthalpies reactants products Table 5.3(a) Some Mean Single Bond Enthalpies in kJ mol–1 at 298 K N = N 418 C = C 611 O = O 498 N ≡ N 946 C ≡ C 837 C = N 615 C = O 741 C ≡ N 891 C ≡ O 1070 Table 5.3(b) Some Mean Multiple Bond Enthalpies in kJ mol–1 at 298 K ** If we use enthalpy of bond formation, (Δf Hbond ), which is the enthalpy change when one mole of a particular type of bond is formed from gaseous atom, then Δf H0 = ∑ Δf H0 bonds of products − ∑ Δf H0 bonds of reactants 0 * Note that symbol used for bond dissociation enthalpy and mean bond enthalpy is the same. H 435.8 C 414 347 N 389 293 159 O 464 351 201 138 F 569 439 272 184 155 Si 293 289 - 368 540 176 P 318 264 209 351 490 213 213 S 339 259 - - 327 226 230 213 Cl 431 330 201 205 255 360 331 251 243 Br 368 276 243 - 197 289 272 213 218 192 I 297 238 - 201 - 213 213 - 209 180 151 H C N O F Si P S CI Br I Rationalised 2023-24 THERMODYNAMICS 155 (reactants and products) in the reaction are in gaseous state. (d) Lattice Enthalpy The lattice enthalpy of an ionic compound is the enthalpy change which occurs when one mole of an ionic compound dissociates into its ions in gaseous state. Na Cl s Na g Cl g  -  - ⊠ ⊠ ⊠  ( ) ⊠ ⊠; ΔlatticeH0 = +788 kJ mol–1 Since it is impossible to determine lattice enthalpies directly by experiment, we use an indirect method where we construct an enthalpy diagram called a Born-Haber Cycle (Fig. 5.9). Let us now calculate the lattice enthalpy of Na+Cl– (s) by following steps given below : 1. Na( ) s N → a g( ) , sublimation of sodium metal, ΔsubH0 = 108.4 kJ mol–1 2. Na() () g N  - a g e g( ) - ⊠1 , the ionization of sodium atoms, ionization enthalpy Δi H0 = 496 kJ mol–1 3. 1 2 Cl2( ) g C → l g( ), the dissociation of chlorine, the reaction enthalpy is half the bond dissociation enthalpy. 1 2 ΔbondH0 = 121 kJ mol–1 4. Cl() () g e  -g Cl g( ) ⊠1 electron gained by chlorine atoms. The electron gain enthalpy, ΔegH 0 = − 348.6 kJ mol–1. You have learnt about ionization enthalpy and electron gain enthalpy in Unit 3. In fact, these terms have been taken from thermodynamics. Earlier terms, ionization energy and electron affinity were in practice in place of the above terms (see the box for justification). Fig. 5.9 Enthalpy diagram for lattice enthalpy of NaCl 5. Na (g) Cl (g) Na Cl (s) + − +− + → The sequence of steps is shown in Fig. 5.9, and is known as a Born-Haber Ionization Energy and Electron Affinity Ionization energy and electron affinity are defined at absolute zero. At any other temperature, heat capacities for the reactants and the products have to be taken into account. Enthalpies of reactions for M(g) → M+(g) + e− (for ionization) M(g) + e− → M− (g) (for electron gain) at temperature, T is Δr H0(T ) = Δr H0(0) + T 0 ∫ Δr CP 0dT The value of Cp for each species in the above reaction is 5/2 R (CV = 3/2R) So, Δr Cp 0 = + 5/2 R (for ionization) Δr Cp 0 = − 5/2 R (for electron gain) Therefore, Δr H0 (ionization enthalpy) = E0 (ionization energy) + 5/2 RT Δr H0 (electron gain enthalpy) = − A( electron affinity) − 5/2 RT Rationalised 2023-24 156 chemIstry The enthalpy of solution of AB(s), ΔsolH0, in water is, therefore, determined by the selective values of the lattice enthalpy, ΔlatticeH0 and enthalpy of hydration of ions, ΔhydH0 as Δsol

$H^0 = \Delta_{lattice}H^0 + \Delta_{hyd}H^0$ For most of the ionic compounds, $\Delta_{sol}H^0$ is positive and the dissociation process is endothermic. Therefore the solubility of most salts in water increases with rise of temperature. If the lattice enthalpy is very high, the dissolution of the compound may not take place at all. Why do many fluorides tend to be less soluble than the corresponding chlorides? Estimates of the magnitudes of enthalpy changes may be made by using tables of bond energies (enthalpies) and lattice energies (enthalpies). (f) Enthalpy of Dilution It is known that enthalpy of solution is the enthalpy change associated with the addition of a specified amount of solute to the specified amount of solvent at a constant temperature and pressure. This argument can be applied to any solvent with slight modification. Enthalpy change for dissolving one mole of gaseous hydrogen chloride in 10 mol of water can be represented by the following equation. For convenience we will use the symbol aq. for water HCl(g) + 10 aq. → HCl.10 aq. ΔH = −69.01 kJ / mol Let us consider the following set of enthalpy changes: (S-1) HCl(g) + 25 aq. → HCl.25 aq. ΔH = −72.03 kJ / mol (S-2) HCl(g) + 40 aq. → HCl.40 aq. ΔH = −72.79 kJ / mol (S-3) HCl(g) + ∞ aq. → HCl. ∞ aq. ΔH = −74.85 kJ / mol The values of ΔH show general dependence of the enthalpy of solution on amount of solvent. As more and more solvent is used, the enthalpy of solution approaches a limiting value, i.e, the value in infinitely dilute solution. For hydrochloric acid this value of ΔH is given above in equation (S-3). cycle. The importance of the cycle is that, the sum of the enthalpy changes round a cycle is zero. Applying Hess's law, we get, $\Delta_{lattice}H^0 = 411.2 + 108.4 + 121 + 496 − 348.6$ $\Delta_{lattice}H^0 = + 788$ kJ for NaCl(s) $\delta$ Na+(g) + Cl− (g) Internal energy is smaller by 2RT (because Δng = 2) and is equal to + 783 kJ mol−1. Now we use the value of lattice enthalpy to calculate enthalpy of solution from the expression: $\Delta_{sol}H^0 = \Delta_{lattice}H^0 + \Delta_{hyd}H^0$ For one mole of NaCl(s), lattice enthalpy = + 788 kJ mol−1 and $\Delta_{hyd}H^0$ = − 784 kJ mol−1( from the literature) $\Delta_{sol}H^0$ = + 788 kJ mol−1 − 784 kJ mol−1 = + 4 kJ mol−1 The dissolution of NaCl(s) is accompanied by very little heat change. (e) Enthalpy of Solution (symbol : $\Delta_{sol}H^0$ ) Enthalpy of solution of a substance is the enthalpy change when one mole of it dissolves in a specified amount of solvent. The enthalpy of solution at infinite dilution is the enthalpy change observed on dissolving the substance in an infinite amount of solvent when the interactions between the ions (or solute molecules) are negligible. When an ionic compound dissolves in a solvent, the ions leave their ordered positions on the crystal lattice. These are now more free in solution. But solvation of these ions (hydration in case solvent is water) also occurs at the same time. This is shown diagrammatically, for an ionic compound, AB (s) Rationalised 2023-24 THERMODYNAMICS 157 If we subtract the first equation (equation S-1) from the second equation (equation S-2) in the above set of equations, we obtain– HCl.25 aq. + 15 aq. → HCl.40 aq. ΔH = [ −72.79 − (−72.03)] kJ / mol = − 0.76 kJ / mol This value (−0.76kJ/mol) of ΔH is enthalpy of dilution. It is the heat withdrawn from the surroundings when additional solvent is added to the solution. The enthalpy of dilution of a solution is dependent on the original concentration of the solution and the amount of solvent added. 5.6 spontaneity The first law of thermodynamics tells us about the relationship between the heat absorbed and the work performed on or by a system. It puts no restrictions on the direction of heat flow. However, the flow of heat is unidirectional from higher temperature to lower temperature. In fact, all naturally occurring processes whether chemical or physical will tend to proceed spontaneously in one direction only. For example, a gas expanding to fill the available volume, burning carbon in dioxygen giving carbon dioxide. But heat will not flow from colder body to warmer body on its own, the gas in a container will not spontaneously contract into one corner or carbon dioxide will not form carbon and dioxygen spontaneously. These and many other spontaneously occurring changes show unidirectional change. We may ask 'what is the driving force of spontaneously occurring changes ? What determines the direction of a spontaneous change ? In this section, we shall establish some criterion for these processes whether these will take place or not. Let us first understand what do we mean by spontaneous reaction or change ? You may think by your common observation that spontaneous reaction is one which occurs immediately when contact is

made between the reactants. Take the case of combination of hydrogen and oxygen. These gases may be mixed at room temperature and left for many years without observing any perceptible change. Although the reaction is taking place between them, it is at an extremely slow rate. It is still called spontaneous reaction. So spontaneity means 'having the potential to proceed without the assistance of external agency'. However, it does not tell about the rate of the reaction or process. Another aspect of spontaneous reaction or process, as we see is that these cannot reverse their direction on their own. We may summarise it as follows: A sp on tan e ou s p r o c e s s i s an irreversible process and may only be reversed by some external agency. (a) Is Decrease in Enthalpy a Criterion for Spontaneity ? If we examine the phenomenon like flow of water down hill or fall of a stone on to the ground, we find that there is a net decrease in potential energy in the direction of change. By analogy, we may be tempted to state that a chemical reaction is spontaneous in a given direction, because decrease in energy has taken place, as in the case of exothermic reactions. For example: 1 2 $N_2$(g) + $H_2$(g) = $NH_3$(g); $\Delta_r H_0$ = − 46.1 kJ mol–1 1 2 $H_2$(g) + 1 2 $Cl_2$(g) = HCl (g); $\Delta_r H_0$ = − 92.32 kJ mol–1 $H_2$(g) + 1 2 $O_2$(g) → $H_2O$(l) ; $\Delta_r H_0$ = −285.8 kJ mol–1 The decrease in enthalpy in passing from reactants to products may be shown for any exothermic reaction on an enthalpy diagram as shown in Fig. 5.10(a). Thus, the postulate that driving force for a chemical reaction may be due to decrease in energy sounds 'reasonable' as the basis of evidence so far ! Now let us examine the following reactions: 1 2 $N_2$(g) + $O_2$(g) → $NO_2$(g); $\Delta_r H_0$ = +33.2 kJ mol–1 C(graphite, s) + 2 S(l) → $CS_2$(l); $\Delta_r H_0$ = +128.5 kJ mol–1 Rationalised 2023-24 158 chemIstry These reactions though endothermic, are spontaneous. The increase in enthalpy may be represented on an enthalpy diagram as shown in Fig. 5.10(b). Fig. 5.10 (a) Enthalpy diagram for exothermic reactions Fig. 5.10 (b) Enthalpy diagram for endothermic reactions Fig. 5.11 Diffusion of two gases respectively and separated by a movable partition [Fig. 5.11 (a)]. When the partition is withdrawn [Fig. 5.11(b)], the gases begin to diffuse into each other and after a period of time, diffusion will be complete. Let us examine the process. Before partition, if we were to pick up the gas molecules from left container, we would be sure that these will be molecules of gas A and similarly if we were to pick up the gas molecules from right container, we would be sure that these will be molecules of gas B. But, if we were to pick up molecules from container when partition is removed, we are not sure whether the molecules picked are of gas A or gas B. We say that the system has become less predictable or more chaotic. We may now formulate another postulate: in an isolated system, there is always a tendency for the systems' energy to become more disordered or chaotic and this could be a criterion for spontaneous change ! At this point, we introduce another thermodynamic function, entropy denoted as S. The above mentioned disorder is the manifestation of entropy. To form a mental Therefore, it becomes obvious that while decrease in enthalpy may be a contributory factor for spontaneity, but it is not true for all cases. (b) Entropy and Spontaneity Then, what drives the spontaneous process in a given direction ? Let us examine such a case in which ΔH = 0 i.e., there is no change in enthalpy, but still the process is spontaneous. Let us consider diffusion of two gases into each other in a closed container which is isolated from the surroundings as shown in Fig. 5.11. The two gases, say, gas A and gas B are represented by black dots and white dots Rationalised 2023-24 THERMODYNAMICS 159 picture, one can think of entropy as a measure of the degree of randomness or disorder in the system. The greater the disorder in an isolated system, the higher is the entropy. As far as a chemical reaction is concerned, this entropy change can be attributed to rearrangement of atoms or ions from one pattern in the reactants to another (in the products). If the structure of the products is very much disordered than that of the reactants, there will be a resultant increase in entropy. The change in entropy accompanying a chemical reaction may be estimated qualitatively by a consideration of the structures of the species taking part in the reaction. Decrease of regularity in structure would mean increase in entropy. For a given substance, the crystalline solid state is the state of lowest entropy (most ordered), The gaseous state is state of highest entropy. Now let us try to quantify entropy. One

way to calculate the degree of disorder or chaotic distribution of energy among molecules would be through statistical method which is beyond the scope of this treatment. Other way would be to relate this process to the heat involved in a process which would make entropy a thermodynamic concept. Entropy, like any other thermodynamic property such as internal energy U and enthalpy H is a state function and ΔS is independent of path. Whenever heat is added to the system, it increases molecular motions causing increased randomness in the system. Thus heat (q) has randomising influence on the system. Can we then equate ΔS with q ? Wait ! Experience suggests us that the distribution of heat also depends on the temperature at which heat is added to the system. A system at higher temperature has greater randomness in it than one at lower temperature. Thus, temperature is the measure of average chaotic motion of particles in the system. Heat added to a system at lower temperature causes greater randomness than when the same quantity of heat is added to it at higher temperature. This suggests that the entropy change is inversely proportional to the temperature. ΔS is related with q and T for a reversible reaction as : $\Delta S = \frac{q_{rev}}{T}$ (5.18) The total entropy change (ΔStotal) for the system and surroundings of a spontaneous process is given by $\Delta S_{total} = \Delta S_{system} + \Delta S_{surr} > 0$ (5.19) When a system is in equilibrium, the entropy is maximum, and the change in entropy, ΔS = 0. We can say that entropy for a spontaneous process increases till it reaches maximum and at equilibrium the change in entropy is zero. Since entropy is a state property, we can calculate the change in entropy of a reversible process by $\Delta S_{sys} = \frac{q_{sys,rev}}{T}$ We find that both for reversible and irreversible expansion for an ideal gas, under isothermal conditions, ΔU = 0, but ΔStotal i.e., $\Delta S_{sys} + \Delta S_{surr}$ is not zero for irreversible process. Thus, ΔU does not discriminate between reversible and irreversible process, whereas ΔS does. Problem 5.10 Predict in which of the following, entropy increases/decreases : (i) A liquid crystallizes into a solid. (ii) Temperature of a crystalline solid is raised from 0 K to 115 K. iii $NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g)$ (iv) $H_2(g) \rightarrow 2H(g)$ Solution (i) After freezing, the molecules attain an ordered state and therefore, entropy decreases. (ii) At 0 K, the contituent particles are static and entropy is minimum. If temperature is raised to 115 K, these begin to move and oscillate Rationalised 2023-24 160 chemIstry about their equilibrium positions in the lattice and system becomes more disordered, therefore entropy increases. (iii) Reactant, NaHCO3 is a solid and it has low entropy. Among products there are one solid and two gases. Therefore, the products represent a condition of higher entropy. (iv) Here one molecule gives two atoms i.e., number of particles increases leading to more disordered state. Two moles of H atoms have higher entropy than one mole of dihydrogen molecule. Problem 5.11 For oxidation of iron, $4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$ entropy change is – 549.4 JK–1 mol–1 at 298 K. Inspite of negative entropy change of this reaction, why is the reaction spontaneous? (Δr H0 for this reaction is –1648 × 103 J mol–1) Solution One decides the spontaneity of a reaction by considering $\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr}$. For calculating ΔSsurr, we have to consider the heat absorbed by the surroundings which is equal to – Δr H 0. At temperature T, entropy change of the surroundings is $\Delta S_{surr} = -\frac{\Delta_r H^0}{T} = -\frac{(-1648 \times 10^3)}{298}$ Jmol K = 5530 JK–1mol–1 Thus, total entropy change for this reaction $\Delta_r S_{total} = 5530 + (-549.4)$ JK–1 mol–1 = 4980.6 JK–1 mol–1 This shows that the above reaction is spontaneous. (c) Gibbs Energy and Spontaneity We have seen that for a system, it is the total entropy change, ΔStotal which decides the spontaneity of the process. But most of the chemical reactions fall into the category of either closed systems or open systems. Therefore, for most of the chemical reactions there are changes in both enthalpy and entropy. It is clear from the discussion in previous sections that neither decrease in enthalpy nor increase in entropy alone can determine the direction of spontaneous change for these systems. For this purpose, we define a new thermodynamic function the Gibbs energy or Gibbs function, G, as G = H – TS (5.20) Gibbs function, G is an extensive property and a state function. The change in Gibbs energy for the system, ΔGsys can be written as $\Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys} - S_{sys}\Delta T$ At constant temperature, $\Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys}$ Usually the subscript 'system' is dropped and we simply write this equation as $\Delta G = \Delta H - T\Delta S$ (5.21)

Thus, Gibbs energy change = enthalpy change – temperature × entropy change, and is referred to as the Gibbs equation, one of the most important equations in chemistry. Here, we have considered both terms together for spontaneity: energy (in terms of $\Delta H$) and entropy ($\Delta S$, a measure of disorder) as indicated earlier. Dimensionally if we analyse, we find that $\Delta G$ has units of energy because, both $\Delta H$ and the $T\Delta S$ are energy terms, since $T\Delta S = (K) (J/K) = J$. Now let us consider how $\Delta G$ is related to reaction spontaneity.

We know,

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr}$$

If the system is in thermal equilibrium with the surrounding, then the temperature of the surrounding is same as that of the system. Also, increase in enthalpy of the surrounding is equal to decrease in the enthalpy of the system. Therefore, entropy change of surroundings,

$$\Delta S_{surr} = \frac{\Delta H_{surr}}{T} = -\frac{\Delta H_{sys}}{T}$$

$$\Delta S_{total} = \Delta S_{sys} + \left(-\frac{\Delta H_{sys}}{T}\right)$$

Rearranging the above equation:

$$T\Delta S_{total} = T\Delta S_{sys} - \Delta H_{sys}$$

For spontaneous process, $\Delta S_{total} > 0$ , so

$$T\Delta S_{sys} - \Delta H_{sys} > 0$$

$$-(\Delta H_{sys} - T\Delta S_{sys}) > 0$$

Using equation 5.21, the above equation can be written as

$$-\Delta G > 0$$

$$\Delta G = \Delta H - T\Delta S < 0 \quad (5.22)$$

$\Delta H_{sys}$ is the enthalpy change of a reaction, $T\Delta S_{sys}$ is the energy which is not available to do useful work. So $\Delta G$ is the net energy available to do useful work and is thus a measure of the 'free energy'. For this reason, it is also known as the free energy of the reaction. $\Delta G$ gives a criteria for spontaneity at constant pressure and temperature. (i) If $\Delta G$ is negative (< 0), the process is spontaneous. (ii) If $\Delta G$ is positive (> 0), the process is non spontaneous. Note : If a reaction has a positive enthalpy change and positive entropy change, it can be spontaneous when $T\Delta S$ is large enough to outweigh $\Delta H$. This can happen in two ways; (a) The positive entropy change of the system can be 'small' in which case T must be large. (b) The positive entropy change of the system can be 'large', in which case T may be small. The former is one of the reasons why reactions are often carried out at high temperature. Table 5.4 summarises the effect of temperature on spontaneity of reactions.

(d) Entropy and Second Law of Thermodynamics We know that for an isolated system the change in energy remains constant. Therefore, increase in entropy in such systems is the natural direction of a spontaneous change. This, in fact is the second law of thermodynamics. Like first law of thermodynamics, second law can also be stated in several ways. The second law of thermodynamics explains why spontaneous exothermic reactions are so common. In exothermic reactions heat released by the reaction increases the disorder of the surroundings and overall entropy change is positive which makes the reaction spontaneous.

(e) Absolute Entropy and Third Law of Thermodynamics Molecules of a substance may move in a straight line in any direction, they may spin like a top and the bonds in the molecules may stretch and compress. These motions of the molecule are called translational, rotational and vibrational motion respectively. When temperature of the system rises, these motions become more vigorous and entropy increases. On the other hand when temperature is lowered, the entropy decreases. The entropy of any pure crystalline substance approaches zero as the temperature approaches absolute zero. This is called third law of thermodynamics. This is so because there is perfect order in a crystal at absolute zero. The statement is confined to pure crystalline solids because theoretical arguments and practical evidences have shown that entropy of solutions and super cooled liquids is not zero at 0 K. The importance of the third law lies in the fact that it permits the calculation of absolute values of entropy of pure substance from thermal data alone. For a pure substance, this can

Table 5.4 Effect of Temperature on Spontaneity of Reactions

| $\Delta_r H^0$ | $\Delta_r S^0$ | $\Delta_r G^0$ | Description* |
|---|---|---|---|
| – | + | – | Reaction spontaneous at all temperatures |
| – | – | – (at low T ) | Reaction spontaneous at low temperature |
| – | – | + (at high T ) | Reaction nonspontaneous at high temperature |
| + | + | + (at low T ) | Reaction nonspontaneous at low temperature |
| + | + | – (at high T ) | Reaction spontaneous at high temperature |
| + | – | + (at all T ) | Reaction nonspontaneous at all temperatures |

* The term low temperature and high temperature are relative. For a particular reaction, high temperature could even mean room temperature.

be done by summing $\frac{q_{rev}}{T}$ increments from 0 K to 298 K. Standard entropies can be used to calculate standard entropy changes by a Hess's law type of calculation.

5.7 Gibbs energy change and equilibrium We have seen how a

knowledge of the sign and magnitude of the free energy change of a chemical reaction allows: (i) Prediction of the spontaneity of the chemical reaction. (ii) Prediction of the useful work that could be extracted from it. So far we have considered free energy changes in irreversible reactions. Let us now examine the free energy changes in reversible reactions. 'Reversible' under strict thermodynamic sense is a special way of carrying out a process such that system is at all times in perfect equilibrium with its surroundings. When applied to a chemical reaction, the term 'reversible' indicates that a given reaction can proceed in either direction simultaneously, so that a dynamic equilibrium is set up. This means that the reactions in both the directions should proceed with a decrease in free energy, which seems impossible. It is possible only if at equilibrium the free energy of the system is minimum. If it is not, the system would spontaneously change to configuration of lower free energy. So, the criterion for equilibrium A + B $\lambda$ C + D; is $\Delta_r G = 0$ Gibbs energy for a reaction in which all reactants and products are in standard state, $\Delta_r G^0$ is related to the equilibrium constant of the reaction as follows: $0 = \Delta_r G^0 + RT \ln K$ or $\Delta_r G^0 = -RT \ln K$ or $\Delta_r G^0 = -2.303\ RT \log K$ (5.23) We also know that (5.24) For strongly endothermic reactions, the value of $\Delta_r H^0$ may be large and positive. In such a case, value of K will be much smaller than 1 and the reaction is unlikely to form much product. In case of exothermic reactions, $\Delta_r H^0$ is large and negative, and $\Delta_r G^0$ is likely to be large and negative too. In such cases, K will be much larger than 1. We may expect strongly exothermic reactions to have a large K, and hence can go to near completion. $\Delta_r G^0$ also depends upon $\Delta_r S^0$, if the changes in the entropy of reaction is also taken into account, the value of K or extent of chemical reaction will also be affected, depending upon whether $\Delta_r S^0$ is positive or negative. Using equation (5.24), Rationalised 2023-24 THERMODYNAMICS 163 (i) It is possible to obtain an estimate of $\Delta G^0$ from the measurement of $\Delta H^0$ and $\Delta S^0$, and then calculate K at any temperature for economic yields of the products. (ii) If K is measured directly in the laboratory, value of $\Delta G^0$ at any other temperature can be calculated. Using equation (5.24), $= - \ldots$ 13 6 10 2 303 8 314 298 3 - ⬚ - ⬚ - ⬚ J mol JK mol K $^{-1}$ $^{-1}$ $^{-1}$ = 2.38 Hence K = antilog 2.38 = 2.4 × 10² . Problem 5.14 At 60°C, dinitrogen tetroxide is 50 per cent dissociated. Calculate the standard free energy change at this temperature and at one atmosphere. Solution $N_2O_4(g)$ $2NO_2(g)$ If $N_2O_4$ is 50% dissociated, the mole fraction of both the substances is given by x x N O NO 2 4 2 1 0 5 1 0 5 2 0 5 1 0 5 - ⬚ ⬚⬚ . . : . . p p N O2 4 NO2 0 5 1 5 1 1 1 5 1 - - . . . atm, atm. The equilibrium constant $K_p$ is given by $K_p = \dfrac{p\ p}{NO\ N\ O}$ 2 2 4 - ⬚ 2 2 1 5 15 05 . ( . ) ( . ) = 1.33 atm. Since $\Delta_r G^0 = -RT \ln K_p$ $\Delta_r G^0 = (-8.314\ JK^{-1}\ mol^{-1}) \times (333\ K) \times (2.303) \times (0.1239) = -763.8\ kJ\ mol^{-1}$ Problem 5.12 Calculate $\Delta_r G^0$ for conversion of oxygen to ozone, $3/2\ O_2(g) \rightarrow O_3(g)$ at 298 K. if $K_p$ for this conversion is $2.47 \times 10^{-29}$. Solution We know $\Delta_r G^0 = -2.303\ RT \log K_p$ and $R = 8.314\ JK^{-1}\ mol^{-1}$ Therefore, $\Delta_r G^0 = -2.303\ (8.314\ J\ K^{-1}\ mol^{-1}) \times (298\ K)\ (\log 2.47 \times 10^{-29}) = 163000\ J\ mol^{-1} = 163\ kJ\ mol^{-1}$. Problem 5.13 Find out the value of equilibrium constant for the following reaction at 298 K. Standard Gibbs energy change, $\Delta_r G^0$ at the given temperature is $-13.6\ kJ\ mol^{-1}$. Solution We know, log K = Rationalised 2023-24 164 chemIstry Summary Thermodynamics deals with energy changes in chemical or physical processes and enables us to study these changes quantitatively and to make useful predictions. For these purposes, we divide the universe into the system and the surroundings. Chemical or physical processes lead to evolution or absorption of heat (q), part of which may be converted into work (w). These quantities are related through the first law of thermodynamics via $\Delta U = q + w$. $\Delta U$, change in internal energy, depends on initial and final states only and is a state function, whereas q and w depend on the path and are not the state functions. We follow sign conventions of q and w by giving the positive sign to these quantities when these are added to the system. We can measure the transfer of heat from one system to another which causes the change in temperature. The magnitude of rise in temperature depends on the heat capacity (C) of a substance. Therefore, heat absorbed or evolved is $q = C\Delta T$. Work can be measured by $w = -p_{ex}\Delta V$, in case of expansion of gases.

Under reversible process, we can put pex = p for infinitesimal changes in the volume making wrev = − p dV. In this condition, we can use gas equation, pV = nRT. At constant volume, w = 0, then ΔU = qV , heat transfer at constant volume. But in study of chemical reactions, we usually have constant pressure. We define another state function enthalpy. Enthalpy change, ΔH = ΔU + Δng RT, can be found directly from the heat changes at constant pressure, ΔH = qp. There are varieties of enthalpy changes. Changes of phase such as melting, vaporization and sublimation usually occur at constant temperature and can be characterized by enthalpy changes which are always positive. Enthalpy of formation, combustion and other enthalpy changes can be calculated using Hess's law. Enthalpy change for chemical reactions can be determined by   r i f i f f i H a - 🔲🔲 🔲 H b products 🔲 🔲🔲 🔲 Hreactions and in gaseous state by Δr H0 = Σ bond enthalpies of the reactants − Σ bond enthalpies of the products First law of thermodynamics does not guide us about the direction of chemical reactions i.e., what is the driving force of a chemical reaction. For isolated systems, ΔU = 0. We define another state function, S, entropy for this purpose. Entropy is a measure of disorder or randomness. For a spontaneous change, total entropy change is positive. Therefore, for an isolated system, ΔU = 0, ΔS > 0, so entropy change distinguishes a spontaneous change, while energy change does not. Entropy changes can be measured by the equation ΔS = qrev T for a reversible process. qrev T is independent of path. Chemical reactions are generally carried at constant pressure, so we define another state function Gibbs energy, G, which is related to entropy and enthalpy changes of the system by the equation: Δr G = Δr H − T Δr S For a spontaneous change, ΔGsys < 0 and at equilibrium, ΔGsys = 0. Standard Gibbs energy change is related to equilibrium constant by Δr G0 = − RT ln K. K can be calculated from this equation, if we know Δr G0 which can be found from . Temperature is an important factor in the equation. Many reactions which are non-spontaneous at low temperature, are made spontaneous at high temperature for systems having positive entropy of reaction. Rationalised 2023-24 THERMODYNAMICS 165 Exercises 5.1 Choose the correct answer. A thermodynamic state function is a quantity (i) used to determine heat changes (ii) whose value is independent of path (iii) used to determine pressure volume work (iv) whose value depends on temperature only. 5.2 For the process to occur under adiabatic conditions, the correct condition is: (i) ΔT = 0 (ii) Δp = 0 (iii) q = 0 (iv) w = 0 5.3 The enthalpies of all elements in their standard states are: (i) unity (ii) zero (iii) < 0 (iv) different for each element 5.4 ΔU 0 of combustion of methane is − X kJ mol−1. The value of ΔH0 is (i) = ΔU 0 (ii) > ΔU 0 (iii) < ΔU 0 (iv) = 0 5.5 The enthalpy of combustion of methane, graphite and dihydrogen at 298 K are, −890.3 kJ mol−1 −393.5 kJ mol−1, and −285.8 kJ mol−1 respectively. Enthalpy of formation of CH4(g) will be (i) −74.8 kJ mol−1 (ii) −52.27 kJ mol−1 (iii) +74.8 kJ mol−1 (iv) +52.26 kJ mol−1. 5.6 A reaction, A + B → C + D + q is found to have a positive entropy change. The reaction will be (i) possible at high temperature (ii) possible only at low temperature (iii) not possible at any temperature (v) possible at any temperature 5.7 In a process, 701 J of heat is absorbed by a system and 394 J of work is done by the system. What is the change in internal energy for the process? 5.8 The reaction of cyanamide, NH2CN (s), with dioxygen was carried out in a bomb calorimeter, and ΔU was found to be −742.7 kJ mol−1 at 298 K. Calculate enthalpy change for the reaction at 298 K. NH2CN(g) + 3 2 O2(g) → N2(g) + CO2(g) + H2O(l) Rationalised 2023-24 166 chemIstry 5.9 Calculate the number of kJ of heat necessary to raise the temperature of 60.0 g of aluminium from 35°C to 55°C. Molar heat capacity of Al is 24 J mol−1 K−1. 5.10 Calculate the enthalpy change on freezing of 1.0 mol of water at10.0°C to ice at −10.0°C. ΔfusH = 6.03 kJ mol−1 at 0°C. Cp [H2O(l)] = 75.3 J mol−1 K−1 Cp [H2O(s)] = 36.8 J mol−1 K−1 5.11 Enthalpy of combustion of carbon to CO2 is −393.5 kJ mol−1. Calculate the heat released upon formation of 35.2 g of CO2 from carbon and dioxygen gas. 5.12 Enthalpies of formation of CO(g), CO2(g), N2O(g) and N2O4(g) are −110, − 393, 81 and 9.7 kJ mol−1 respectively. Find the value of Δr H for the reaction: N2O4(g) + 3CO(g) → N2O(g) + 3CO2(g) 5.13 Given N2(g) + 3H2(g) → 2NH3(g); Δr H0 = −92.4

kJ mol–1 What is the standard enthalpy of formation of NH3 gas? 5.14 Calculate the standard enthalpy of formation of CH3OH(l) from the following data: CH3OH (l) + 3 2 O2(g) → CO2(g) + 2H2O(l) ; Δr H0 = –726 kJ mol–1 C(graphite) + O2(g) → CO2(g) ; Δc H0 = –393 kJ mol–1 H2(g) + 1 2 O2(g) → H2O(l); Δf H0 = –286 kJ mol–1. 5.15 Calculate the enthalpy change for the process CCl4(g) → C(g) + 4 Cl(g) and calculate bond enthalpy of C – Cl in CCl4(g). ΔvapH0(CCl4) = 30.5 kJ mol–1. Δf H0 (CCl4) = –135.5 kJ mol–1. ΔaH0 (C) = 715.0 kJ mol–1, where ΔaH0 is enthalpy of atomisation ΔaH0 (Cl2) = 242 kJ mol–1 5.16 For an isolated system, ΔU = 0, what will be ΔS ? 5.17 For the reaction at 298 K, 2A + B → C ΔH = 400 kJ mol–1 and ΔS = 0.2 kJ K–1 mol–1 At what temperature will the reaction become spontaneous considering ΔH and ΔS to be constant over the temperature range. 5.18 For the reaction, 2 Cl(g) → Cl2(g), what are the signs of ΔH and ΔS ? 5.19 For the reaction 2 A(g) + B(g) → 2D(g) ΔU 0 = –10.5 kJ and ΔS0 = –44.1 JK–1. Calculate ΔG0 for the reaction, and predict whether the reaction may occur spontaneously. Rationalised 2023-24 THERMODYNAMICS 167 5.20 The equilibrium constant for a reaction is 10. What will be the value of ΔG0 ? R = 8.314 JK–1 mol–1, T = 300 K. 5.21 Comment on the thermodynamic stability of NO(g), given 1 2 N2(g) + 1 2 O2(g) → NO(g); Δr H0 = 90 kJ mol–1 NO(g) + 1 2 O2(g) → NO2(g): Δr H0= –74 kJ mol–1 5.22 Calculate the entropy change in surroundings when 1.00 mol of H2O(l) is formed under standard conditions. Δf H0 = –286 kJ mol–1. Rationalised 2023-24Unit 6 Equilibrium Chemical equilibria are important in numerous biological and environmental processes. For example, equilibria involving O2 molecules and the protein hemoglobin play a crucial role in the transport and delivery of O2 from our lungs to our muscles. Similar equilibria involving CO molecules and hemoglobin account for the toxicity of CO. When a liquid evaporates in a closed container, molecules with relatively higher kinetic energy escape the liquid surface into the vapour phase and number of liquid molecules from the vapour phase strike the liquid surface and are retained in the liquid phase. It gives rise to a constant vapour pressure because of an equilibrium in which the number of molecules leaving the liquid equals the number returning to liquid from the vapour. We say that the system has reached equilibrium state at this stage. However, this is not static equilibrium and there is a lot of activity at the boundary between the liquid and the vapour. Thus, at equilibrium, the rate of evaporation is equal to the rate of condensation. It may be represented by H2O (l) H2O (vap) The double half arrows indicate that the processes in both the directions are going on simultaneously. The mixture of reactants and products in the equilibrium state is called an equilibrium mixture. Equilibrium can be established for both physical processes and chemical reactions. The reaction may be fast or slow depending on the experimental conditions and the nature of the reactants. When the reactants in a closed vessel at a particular temperature react to give products, the concentrations of the reactants keep on decreasing, while those of products keep on increasing for some time after which there is no change in the concentrations of either of the reactants or products. This stage of the system is the dynamic equilibrium and the rates of the forward and reverse reactions become equal. It is due to After studying this unit you will be able to • identify dynamic nature of equilibrium involved in physical and chemical processes; • state the law of equilibrium; • explain characteristics of equilibria involved in physical and chemical processes; • write expressions for equilibrium constants; • establish a relationship between Kp and Kc ; • explain various factors that affect the equilibrium state of a reaction; • classify substances as acids or bases according to Arrhenius, Bronsted-Lowry and Lewis concepts; • classify acids and bases as weak or strong in terms of their ionization constants; • explain the dependence of degree of ionization on concentration of the electrolyte and that of the common ion; • describe pH scale for representing hydrogen ion concentration; • explain ionisation of water and its duel role as acid and base; • describe ionic product (Kw ) and pKw for water; • appreciate use of buffer solutions; • calculate solubility product constant. Rationalised 2023-24 EQUILIBRIUM 169 this dynamic equilibrium stage that there is no change in the concentrations of various species in the

reaction mixture. Based on the extent to which the reactions proceed to reach the state of chemical equilibrium, these may be classified in three groups. (i) The reactions that proceed nearly to completion and only negligible concentrations of the reactants are left. In some cases, it may not be even possible to detect these experimentally. (ii) The reactions in which only small amounts of products are formed and most of the reactants remain unchanged at equilibrium stage. (iii) The reactions in which the concentrations of the reactants and products are comparable, when the system is in equilibrium. The extent of a reaction in equilibrium varies with the experimental conditions such as concentrations of reactants, temperature, etc. Optimisation of the operational conditions is very important in industry and laboratory so that equilibrium is favorable in the direction of the desired product. Some important aspects of equilibrium involving physical and chemical processes are dealt in this unit along with the equilibrium involving ions in aqueous solutions which is called as ionic equilibrium. 6.1 E Q U IL IBRI U M IN PHYS I C A L PROCESSES The characteristics of system at equilibrium are better understood if we examine some physical processes. The most familiar examples are phase transformation processes, e.g., solid liquid liquid gas solid gas 6.1.1 Solid-Liquid Equilibrium Ice and water kept in a perfectly insulated thermos flask (no exchange of heat between its contents and the surroundings) at 273K and the atmospheric pressure are in equilibrium state and the system shows interesting characteristic features. We observe that the mass of ice and water do not change with time and the temperature remains constant. However, the equilibrium is not static. The intense activity can be noticed at the boundary between ice and water. Molecules from the liquid water collide against ice and adhere to it and some molecules of ice escape into liquid phase. There is no change of mass of ice and water, as the rates of transfer of molecules from ice into water and of reverse transfer from water into ice are equal at atmospheric pressure and 273 K. It is obvious that ice and water are in equilibrium only at particular temperature and pressure. For any pure substance at atmospheric pressure, the temperature at which the solid and liquid phases are at equilibrium is called the normal melting point or normal freezing point of the substance. The system here is in dynamic equilibrium and we can infer the following: (i) Both the opposing processes occur simultaneously. (ii) Both the processes occur at the same rate so that the amount of ice and water remains constant. 6.1.2 Liquid-Vapour Equilibrium This equilibrium can be better understood if we consider the example of a transparent box carrying a U-tube with mercury (manometer). Drying agent like anhydrous calcium chloride (or phosphorus penta-oxide) is placed for a few hours in the box. After removing the drying agent by tilting the box on one side, a watch glass (or petri dish) containing water is quickly placed inside the box. It will be observed that the mercury level in the right limb of the manometer slowly increases and finally attains a constant value, that is, the pressure inside the box increases and reaches a constant value. Also the volume of water in the watch glass decreases (Fig. 6.1). Initially there was no water vapour (or very less) inside the box. As water evaporated the pressure in the box increased due to addition of water molecules into the gaseous phase inside the box. The rate of evaporation is constant. Rationalised 2023-24 170 chemistry However, the rate of increase in pressure decreases with time due to condensation of vapour into water. Finally it leads to an equilibrium condition when there is no net evaporation. This implies that the number of water molecules from the gaseous state into the liquid state also increases till the equilibrium is attained i.e., rate of evaporation= rate of condensation H2O(l) H2O (vap) At equilibrium the pressure exerted by the water molecules at a given temperature remains constant and is called the equilibrium vapour pressure of water (or just vapour pressure of water); vapour pressure of water increases with temperature. If the above experiment is repeated with methyl alcohol, acetone and ether, it is observed that different liquids have different equilibrium vapour pressures at the same temperature, and the liquid which has a higher vapour pressure is more volatile and has a lower boiling point. If we expose three watch glasses containing separately 1mL each of acetone, ethyl alcohol, and water to atmosphere and

repeat the experiment with different volumes of the liquids in a warmer room, it is observed that in all such cases the liquid eventually disappears and the time taken for complete evaporation depends on (i) the nature of the liquid, (ii) the amount of the liquid and (iii) the temperature. When the watch glass is open to the atmosphere, the rate of evaporation remains constant but the molecules are dispersed into large volume of the room. As a consequence the rate of condensation from vapour to liquid state is much less than the rate of evaporation. These are open systems and it is not possible to reach equilibrium in an open system. Water and water vapour are in equilibrium position at atmospheric pressure (1.013 bar) and at 100°C in a closed vessel. The boiling point of water is 100°C at 1.013 bar pressure. For any pure liquid at one atmospheric pressure (1.013 bar), the temperature at which the liquid and vapours are at equilibrium is called normal boiling point of the liquid. Boiling point of the liquid depends on the atmospheric pressure. It depends on the altitude of the place; at high altitude the boiling point decreases. 6.1.3 Solid – Vapour Equilibrium Let us now consider the systems where solids sublime to vapour phase. If we place solid iodine in a closed vessel, after sometime the vessel gets filled up with violet vapour and the intensity of colour increases with time. After certain time the intensity of colour becomes constant and at this stage equilibrium is attained. Hence solid iodine sublimes to give iodine vapour and the iodine vapour condenses to give solid iodine. The equilibrium can be represented as, $I_2$(solid) $I_2$ (vapour) Other examples showing this kind of equilibrium are, Camphor (solid) Camphor (vapour) $NH_4Cl$ (solid) $NH_4Cl$ (vapour) Fig. 6.1 Measuring equilibrium vapour pressure of water at a constant temperature Rationalised 2023-24 EQUILIBRIUM 171 6.1.4 Equilibrium Involving Dissolution of Solid or Gases in Liquids Solids in liquids We know from our experience that we can dissolve only a limited amount of salt or sugar in a given amount of water at room temperature. If we make a thick sugar syrup solution by dissolving sugar at a higher temperature, sugar crystals separate out if we cool the syrup to the room temperature. We call it a saturated solution when no more of solute can be dissolved in it at a given temperature. The concentration of the solute in a saturated solution depends upon the temperature. In a saturated solution, a dynamic equilibrium exits between the solute molecules in the solid state and in the solution: Sugar (solution) Sugar (solid), and the rate of dissolution of sugar = rate of crystallisation of sugar. Equality of the two rates and dynamic nature of equilibrium has been confirmed with the help of radioactive sugar. If we drop some radioactive sugar into saturated solution of non-radioactive sugar, then after some time radioactivity is observed both in the solution and in the solid sugar. Initially there were no radioactive sugar molecules in the solution but due to dynamic nature of equilibrium, there is exchange between the radioactive and non-radioactive sugar molecules between the two phases. The ratio of the radioactive to non-radioactive molecules in the solution increases till it attains a constant value. Gases in liquids When a soda water bottle is opened, some of the carbon dioxide gas dissolved in it fizzes out rapidly. The phenomenon arises due to difference in solubility of carbon dioxide at different pressures. There is equilibrium between the molecules in the gaseous state and the molecules dissolved in the liquid under pressure i.e., $CO_2$ (gas) $CO_2$ (in solution) This equilibrium is governed by Henry's law, which states that the mass of a gas dissolved in a given mass of a solvent at any temperature is proportional to the pressure of the gas above the solvent. This amount decreases with increase of temperature. The soda water bottle is sealed under pressure of gas when its solubility in water is high. As soon as the bottle is opened, some of the dissolved carbon dioxide gas escapes to reach a new equilibrium condition required for the lower pressure, namely its partial pressure in the atmosphere. This is how the soda water in bottle when left open to the air for some time, turns 'flat'. It can be generalised that: (i) For solid liquid equilibrium, there is only one temperature (melting point) at 1 atm (1.013 bar) at which the two phases can coexist. If there is no exchange of heat with the surroundings, the mass of the two phases remains constant. (ii) For liquid vapour equilibrium, the vapour pressure is constant at a given temperature. (iii) For dissolution of solids in liquids, the solubility is constant at a given temperature.

(iv) For dissolution of gases in liquids, the concentration of a gas in liquid is proportional to the pressure (concentration) of the gas over the liquid. These observations are summarised in Table 6.1

Table 6.1 Some Features of Physical Equilibria

| Process | Conclusion |
|---|---|
| Liquid $\rightleftharpoons$ Vapour $H_2O$ (l) $\rightleftharpoons$ $H_2O$ (g) | $p_{H_2O}$ constant at given temperature |
| Solid $\rightleftharpoons$ Liquid $H_2O$ (s) $\rightleftharpoons$ $H_2O$ (l) | Melting point is fixed at constant pressure |
| Solute(s) $\rightleftharpoons$ Solute (solution) Sugar(s) $\rightleftharpoons$ Sugar (solution) | Concentration of solute in solution is constant at a given temperature |
| Gas(g) $\rightleftharpoons$ Gas (aq) $CO_2(g)$ $\rightleftharpoons$ $CO_2(aq)$ | [gas(aq)]/[gas(g)] is constant at a given temperature [$CO_2(aq)$]/[$CO_2(g)$] is constant at a given temperature |

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6.1.5 General Characteristics of Equilibria Involving Physical Processes

For the physical processes discussed above, following characteristics are common to the system at equilibrium:

(i) Equilibrium is possible only in a closed system at a given temperature. (ii) Both the opposing processes occur at the same rate and there is a dynamic but stable condition. (iii) All measurable properties of the system remain constant. (iv) When equilibrium is attained for a physical process, it is characterised by constant value of one of its parameters at a given temperature. Table 6.1 lists such quantities. (v) The magnitude of such quantities at any stage indicates the extent to which the physical process has proceeded before reaching equilibrium.

6.2 EQUILIBRIUM IN CHEMICAL PROCESSES – DYNAMIC EQUILIBRIUM

Analogous to the physical systems chemical reactions also attain a state of equilibrium. These reactions can occur both in forward and backward directions. When the rates of the forward and reverse reactions become equal, the concentrations of the reactants and the products remain constant. This is the stage of chemical equilibrium. This equilibrium is dynamic in nature as it consists of a forward reaction in which the reactants give product(s) and reverse reaction in which product(s) gives the original reactants.

For a better comprehension, let us consider a general case of a reversible reaction,

A + B $\rightleftharpoons$ C + D

With passage of time, there is accumulation of the products C and D and depletion of the reactants A and B (Fig. 6.2). This leads to a decrease in the rate of forward reaction and an increase in the rate of the reverse reaction,

Fig. 6.2 Attainment of chemical equilibrium.

Eventually, the two reactions occur at the same rate and the system reaches a state of equilibrium. Similarly, the reaction can reach the state of equilibrium even if we start with only C and D; that is, no A and B being present initially, as the equilibrium can be reached from either direction.

The dynamic nature of chemical equilibrium can be demonstrated in the synthesis of ammonia by Haber's process. In a series of experiments, Haber started with known amounts of dinitrogen and dihydrogen maintained at high temperature and pressure and at regular intervals determined the amount of ammonia present. He was successful in determining also the concentration of unreacted dihydrogen and dinitrogen. Fig. 6.4 (page 174) shows that after a certain time the composition of the mixture remains the same even though some of the reactants are still present. This constancy in composition indicates that the reaction has reached equilibrium. In order to understand the dynamic nature of the reaction, synthesis of ammonia is carried out with exactly the same starting conditions (of partial pressure and temperature) but using $D_2$ (deuterium) in place of $H_2$. The reaction mixtures starting either with $H_2$ or $D_2$ reach equilibrium with the same composition, except that $D_2$ and $ND_3$ are present instead of $H_2$ and $NH_3$. After

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Dynamic Equilibrium – A Student's Activity

Equilibrium whether in a physical or in a chemical system, is always of dynamic nature. This can be demonstrated by the use of radioactive isotopes. This is not feasible in a school laboratory. However this concept can be easily comprehended by performing the following activity. The activity can be performed in a group of 5 or 6 students. Take two 100mL measuring cylinders (marked as 1 and 2) and two glass tubes each of 30 cm length. Diameter of the tubes may be same or different in the range of 3-5mm. Fill nearly half of the measuring cylinder-1 with coloured water (for this purpose add a crystal of potassium permanganate to water) and keep second cylinder (number 2) empty. Put one tube in cylinder 1 and second in cylinder 2. Immerse one tube in cylinder 1, close its upper tip with a finger and transfer the coloured water contained in its lower portion to cylinder 2. Using

second tube, kept in 2nd cylinder, transfer the coloured water in a similar manner from cylinder 2 to cylinder 1. In this way keep on transferring coloured water using the two glass tubes from cylinder 1 to 2 and from 2 to 1 till you notice that the level of coloured water in both the cylinders becomes constant. If you continue intertransferring coloured solution between the cylinders, there will not be any further change in the levels of coloured water in two cylinders. If we take analogy of 'level' of coloured water with 'concentration' of reactants and products in the two cylinders, we can say the process of transfer, which continues even after the constancy of level, is indicative of dynamic nature of the process. If we repeat the experiment taking two tubes of different diameters we find that at equilibrium the level of coloured water in two cylinders is different. How far diameters are responsible for change in levels in two cylinders? Empty cylinder (2) is an indicator of no product in it at the beginning. Fig.6.3 Demonstrating dynamic nature of equilibrium. (a) initial stage (b) final stage after the equilibrium is attained. 1 2 1 2 (a) (b) Rationalised 2023-24 174 chemistry 2NH3(g) N2(g) + 3H2(g) Similarly let us consider the reaction, H2(g) + I2(g) 2HI(g). If we start with equal initial concentration of H2 and I2, the reaction proceeds in the forward direction and the concentration of H2 and I2 decreases while that of HI increases, until all of these become constant at equilibrium (Fig. 6.5). We can also start with HI alone and make the reaction to proceed in the reverse direction; the concentration of HI will decrease and concentration of H2 and I2 will increase until they all become constant when equilibrium is reached (Fig. 6.5). If total number of H and I atoms are same in a given volume, the same equilibrium mixture is obtained whether we start it from pure reactants or pure product. equilibrium is attained, these two mixtures (H2, N2, NH3 and D2, N2, ND3) are mixed together and left for a while. Later, when this mixture is analysed, it is found that the concentration of ammonia is just the same as before. However, when this mixture is analysed by a mass spectrometer, it is found that ammonia and all deuterium containing forms of ammonia (NH3, NH2D, NHD2 and ND3) and dihydrogen and its deutrated forms (H2, HD and D2) are present. Thus one can conclude that scrambling of H and D atoms in the molecules must result from a continuation of the forward and reverse reactions in the mixture. If the reaction had simply stopped when they reached equilibrium, then there would have been no mixing of isotopes in this way. Use of isotope (deuterium) in the formation of ammonia clearly indicates that chemical reactions reach a state of dynamic equilibrium in which the rates of forward and reverse reactions are equal and there is no net change in composition. Equilibrium can be attained from both sides, whether we start reaction by taking, H2(g) and N2(g) and get NH3(g) or by taking NH3(g) and decomposing it into N2(g) and H2(g). N2(g) + 3H2(g) 2NH3(g) Fig. 6.5 Chemical equilibrium in the reaction H2(g) + I2(g) 2HI(g) can be attained from either direction Fig. 6.4 Depiction of equilibrium for the reaction 6.3 LAW OF CHEMICAL EQUILIBRIUM AND EQUILIBRIUM CONSTANT A mixture of reactants and products in the equilibrium state is called an equilibrium mixture. In this section we shall address a number of important questions about the composition of equilibrium mixtures: What is the relationship between the concentrations of reactants and products in an equilibrium mixture? How can we determine equilibrium concentrations from initial concentrations? What factors can be exploited to alter the N g 2 2 - ⬜ 3 2 H g - NH3 g- Rationalised 2023-24 EQUILIBRIUM 175 composition of an equilibrium mixture? The last question in particular is important when choosing conditions for synthesis of industrial chemicals such as H2, NH3, CaO etc. To answer these questions, let us consider a general reversible reaction: A + B C + D where A and B are the reactants, C and D are the products in the balanced chemical equation. On the basis of experimental studies of many reversible reactions, the Norwegian chemists Cato Maximillian Guldberg and Peter Waage proposed in 1864 that the concentrations in an equilibrium mixture are related by the following equilibrium equation, Kc - ⬜- ⬜ - ⬜- ⬜ C D A B (6.1) (6.1) where Kc is the equilibrium constant and the expression on the right side is called the equilibrium constant expression. The equilibrium equation is also known as the law of mass action because in the early days of chemistry, concentration was called "active mass". In

order to appreciate their work better, let us consider reaction between gaseous H2 and I2 carried out in a sealed vessel at 731K. H2(g) + I2(g) 2HI(g) 1 mol 1 mol 2 mol Six sets of experiments with varying initial conditions were performed, starting with only gaseous H2 and I2 in a sealed reaction vessel in first four experiments (1, 2, 3 and 4) and only HI in other two experiments (5 and 6). Experiment 1, 2, 3 and 4 were performed taking different concentrations of H2 and / or I 2, and with time it was observed that intensity of the purple colour remained constant and equilibrium was attained. Similarly, for experiments 5 and 6, the equilibrium was attained from the opposite direction. Data obtained from all six sets of experiments are given in Table 6.2. It is evident from the experiments 1, 2, 3 and 4 that number of moles of dihydrogen reacted = number of moles of iodine reacted = ½ (number of moles of HI formed). Also, experiments 5 and 6 indicate that, $[H_2(g)]_{eq} = [I_2(g)]_{eq}$ Knowing the above facts, in order to establish a relationship between concentrations of the reactants and products, several combinations can be tried. Let us consider the simple expression, $[HI(g)]_{eq}$ / $[H_2(g)]_{eq}$ $[I_2(g)]_{eq}$ It can be seen from Table 6.3 that if we put the equilibrium concentrations of the reactants and products, the above expression Table 6.2 Initial and Equilibrium Concentrations of H2, I2 and HI Rationalised 2023-24 176 chemistry is far from constant. However, if we consider the expression, $[HI(g)]^2_{eq}$ / $[H_2(g)]_{eq}$ $[I_2(g)]_{eq}$ we find that this expression gives constant value (as shown in Table 6.3) in all the six cases. It can be seen that in this expression the power of the concentration for reactants and products are actually the stoichiometric coefficients in the equation for the chemical reaction. Thus, for the reaction H2(g) + I2(g) 2HI(g), following equation 6.1, the equilibrium constant Kc is written as, $K_c = [HI(g)]_{eq}^2$ / $[H_2(g)]_{eq}$ $[I_2(g)]_{eq}$ (6.2) Generally the subscript 'eq' (used for equilibrium) is omitted from the concentration terms. It is taken for granted that the concentrations in the expression for Kc are equilibrium values. We, therefore, write, $K_c = [HI(g)]^2$ / $[H_2(g)]$ $[I_2(g)]$ (6.3) The subscript 'c' indicates that Kc is expressed in concentrations of mol L−1. At a given temperature, the product of concentrations of the reaction products raised to the respective stoichiometric coefficient in the balanced chemical equation divided by the product of concentrations of the reactants raised to their individual stoichiometric coefficients has a constant value. This is known as the Equilibrium Law or Law of Chemical Equilibrium. The equilibrium constant for a general reaction, a A + b B c C + d D is expressed as, $K_c = [C]^c [D]^d$ / $[A]^a[B]^b$ (6.4) where [A], [B], [C] and [D] are the equilibrium concentrations of the reactants and products. Equilibrium constant for the reaction, 4NH3(g) + 5O2(g) 4NO(g) + 6H2O(g) is written as $K_c = [NO]^4[H_2O]^6$ / $[NH_3]^4 [O_2]^5$ Molar concentration of different species is indicated by enclosing these in square bracket and, as mentioned above, it is implied that these are equilibrium concentrations. While writing expression for equilibrium constant, symbol for phases (s, l, g) are generally ignored. Let us write equilibrium constant for the reaction, H2(g) + I2(g) 2HI(g) (6.5) as, $K_c = [HI]^2$ / $[H_2] [I_2] = x$ (6.6) The equilibrium constant for the reverse reaction, 2HI(g) H2(g) + I2(g), at the same temperature is, $K'_c = [H_2] [I_2]$ / $[HI]^2 = 1/ x = 1 / K_c$ (6.7) Thus, $K'_c = 1 / K_c$ (6.8) Equilibrium constant for the reverse reaction is the inverse of the equilibrium constant for the reaction in the forward direction. If we change the stoichiometric coefficients in a chemical equation by multiplying throughout by a factor then we must make sure that the expression for equilibrium constant also reflects that change. For example, if the reaction (6.5) is written as, ½ H2(g) + ½ I2(g) HI(g) (6.9) the equilibrium constant for the above reaction is given by $K''_c = [HI]$ / $[H_2]^{1/2}[I_2]^{1/2} = \{[HI]^2 / [H_2][I_2]\}^{1/2} = x^{1/2} = K_c^{1/2}$ (6.10) On multiplying the equation (6.5) by n, we get Table 6.3 Expression I n v o l v i n g t h e Equilibrium Concentration of Reactants H2(g) + I2(g) 2HI(g) Rationalised 2023-24 EQUILIBRIUM 177 nH2(g) + nI2(g) D 2nHI(g) (6.11) Therefore, equilibrium constant for the reaction is equal to $K_c^n$. These findings are summarised in Table 6.4. It should be noted that because the equilibrium constants Kc and K'c have different numerical values, it is important to specify the form of the balanced chemical equation when quoting the value of an equilibrium constant. N2(g) + O2(g) 2NO(g) Solution For the reaction equilibrium constant,Kc can be written as, $K_c = NO = 2.8 10 M–3 2 2 2 2 3 3 3 0 10 4 2 10 N$

O . . M M = 0.622 Problem 6.1 The following concentrations were obtained for the formation of NH3 from N2 and H2 at equilibrium at 500K. [N2] = 1.5 × 10–2M. [H2] = 3.0 ×10–2 M and [NH3] = 1.2 ×10–2M. Calculate equilibrium constant. Solution The equilibrium constant for the reaction, N2(g) + 3H2(g) 2NH3(g) can be written as, Kc = = NH g N g H g 3 2 2 2 3 2 2 2 1 2 10 1 5 10 🔲 - 🔲🔲🔲🔲 - 🔲🔲🔲🔲 - 🔲🔲🔲 - 🔲 - 🔲🔲🔲 . . 3 0 10 2 3 - . 🔲🔲 = 0.106 × 104 = 1.06 × 103 Problem 6.2 At equilibrium, the concentrations of N2=3.0 × 10–3M, O2 = 4.2 × 10–3M and NO= 2.8 × 10–3M in a sealed vessel at 800K. What will be Kc for the reaction Table 6.4 Relations between Equilibrium Constants for a General Reaction and its Multiples. Chemical equation Equilibrium constant a A + b B c C + dD Kc c C + d D a A + b B K' c =(1/Kc ) na A + nb B ncC + ndD K''' c = (Kc n ) 6.4 HOMOGENEOUS EQUILIBRIA In a homogeneous system, all the reactants and products are in the same phase. For example, in the gaseous reaction, N2(g) + 3H2(g) 2NH3(g), reactants and products are in the homogeneous phase. Similarly, for the reactions, CH3COOC2H5 (aq) + H2O (l) CH3COOH (aq) + C2H5OH (aq) and, Fe3+ (aq) + SCN– (aq) Fe(SCN)2+ (aq) all the reactants and products are in homogeneous solution phase. We shall now consider equilibrium constant for some homogeneous reactions. 6.4.1 Equilibrium Constant in Gaseous Systems So far we have expressed equilibrium constant of the reactions in terms of molar concentration of the reactants and products, and used symbol, Kc for it. For reactions involving gases, however, it is usually more convenient to express the equilibrium constant in terms of partial pressure. The ideal gas equation is written as, pV = nRT ⇒ p n V = RT Here, p is the pressure in Pa, n is the number of moles of the gas, V is the volume in m3 and T is the temperature in Kelvin Rationalised 2023-24 178 chemistry Therefore, n/V is concentration expressed in mol/m3 If concentration c, is in mol/L or mol/dm3, and p is in bar then p = cRT, We can also write p = [gas]RT. Here, R= 0.0831 bar litre/mol K At constant temperature, the pressure of the gas is proportional to its concentration i.e., p ∝ [gas] For reaction in equilibrium H2(g) + I2(g) 2HI(g) We can write either Kc HI g H g I g = 🔲 ( ) 🔲🔲🔲🔲 ( ) 🔲🔲🔲🔲 ( ) 🔲🔲🔲 2 2 2 or K p p p c HI H I = ( ) ( )( ) 2 2 2 (6.12) Further, since p T p HI I = 🔲HI(g R ) 🔲🔲🔲 2 2 2 2 = 🔲 ( ) 🔲🔲🔲 = 🔲 ( ) 🔲🔲🔲 I g R H H g R T p T Therefore, K p p p T T p = ( ) ( )( ) 🔲 ( ) 🔲🔲🔲 [ ] 🔲 ( ) 🔲🔲🔲🔲 ( ) 🔲🔲🔲 HI H I g g g 2 2 2 2 2 2 = HI R H R I . RT = HI H I g g g 🔲 ( ) 🔲🔲🔲🔲 ( ) 🔲🔲🔲🔲 ( ) 🔲🔲🔲 = 2 2 2 Kc (6.13) In this example, Kp = Kc i.e., both equilibrium constants are equal. However, this is not always the case. For example in reaction N2(g) + 3H2(g) 2NH3(g) Kp = ( ) ( )( ) p p p NH N H 3 2 2 2 3 = 🔲 ( ) 🔲🔲🔲 [ ] 🔲 ( ) 🔲🔲🔲🔲 ( ) 🔲🔲🔲 ( ) NH g R N g R g R 3 3 2 2 2 2 3 T T H. T = 🔲 ( ) 🔲🔲🔲 [ ] 🔲 ( ) 🔲🔲🔲🔲 ( ) 🔲🔲🔲 = ( ) – NH g R – N g g R 3 3 2 2 2 2 T 2 H K T c or K K p c = ( T ) – R 2 (6.14) Similarly, for a general reaction a A + b B c C + d D K p p p p T T p C c D d A a B b c d c d a b a b = ( )( ) ( )( ) = [ ] [ ] ( ) [ ] [ ] ( ) ( + ) ( + ) C D R A B R = [ ] [ ] [ ] [ ] ( ) C D ( + )– + ( ) A B R c d a b c d a b T = [ ] [ ] [ ] [ ] ( ) = ( ) C D A B R R c d a b T Kc T Δ Δ n n (6.15) where Δn = (number of moles of gaseous products) – (number of moles of gaseous reactants) in the balanced chemical equation. It is necessary that while calculating the value of Kp, pressure should be expressed in bar because standard state for pressure is 1 bar. We know from Unit 1 that: 1pascal, Pa=1Nm–2, and 1bar = 105 Pa Kp values for a few selected reactions at different temperatures are given in Table 6.5 Table 6.5 Equilibrium Constants, Kp for a Few Selected Reactions Problem 6.3 PCl5, PCl3 and Cl2 are at equilibrium at 500 K and having concentration 1.59M PCl3, 1.59M Cl2 and 1.41 M PCl5. Rationalised 2023-24 EQUILIBRIUM 179 Calculate Kc for the reaction, PCl5 PCl3 + Cl2 Solution The equilibrium constant Kc for the above reaction can be written as, Kc PCl Cl PCl - 🔲- 🔲 - 🔲 🔲🔲🔲🔲 3 2 5 2 1 59 1 41 1 79 . . . Problem 6.4 The value of Kc = 4.24 at 800K for the reaction, CO (g) + H2O (g) CO2 (g) + H2 (g) Calculate equilibrium concentrations of CO2, H2, CO and H2O at 800 K, if only CO and H2O are present initially at concentrations of 0.10M each. Solution For the reaction, CO (g) + H2O (g) CO2 (g) + H2 (g) Initial concentration: 0.1M 0.1M 0 0 Let x mole per litre of each of the product be formed. At equilibrium: (0.1-x) M (0.1-x) M x M x M where x is the amount of CO2 and H2 at equilibrium. Hence, equilibrium constant can be written as, Kc = x2/(0.1-x)2 = 4.24 x2 = 4.24(0.01 + x2-0.2x) x2 = 0.0424 + 4.24x2-0.848x 3.24x2 – 0.848x + 0.0424 = 0 a = 3.24, b = – 0.848, c = 0.0424 (for quadratic equation

$ax^2 + bx + c = 0$, x $\frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$ x = 0.848±√(0.848)² − 4(3.24)(0.0424)/ (3.24×2) x = (0.848 ± 0.4118)/ 6.48 $x_1$ = (0.848 − 0.4118)/6.48 = 0.067 $x_2$ = (0.848 + 0.4118)/6.48 = 0.194 the value 0.194 should be neglected because it will give concentration of the reactant which is more than initial concentration. Hence the equilibrium concentrations are, [$CO_2$] = [$H_2$-] = x = 0.067 M [CO] = [$H_2O$] = 0.1 − 0.067 = 0.033 M **Problem 6.5** For the equilibrium, $2NOCl(g)$ $2NO(g)$ + $Cl_2(g)$ the value of the equilibrium constant, $K_c$ is 3.75 × 10–6 at 1069 K. Calculate the $K_p$ for the reaction at this temperature? **Solution** We know that, $K_p = K_c (RT)^{\Delta n}$ For the above reaction, $\Delta n$ = (2+1) − 2 = 1 $K_p$ = 3.75 ×10–6 (0.0831 × 1069) $K_p$ = 0.033 **6.5 HETEROGENEOUS EQUILIBRIA** Equilibrium in a system having more than one phase is called heterogeneous equilibrium. The equilibrium between water vapour and liquid water in a closed container is an example of heterogeneous equilibrium. $H_2O(l)$ $H_2O(g)$ In this example, there is a gas phase and a liquid phase. In the same way, equilibrium between a solid and its saturated solution, $Ca(OH)_2 (s)$ + (aq) $Ca^{2+}$ (aq) + 2OH– (aq) is a heterogeneous equilibrium. Heterogeneous equilibria often involve pure solids or liquids. We can simplify equilibrium expressions for the heterogeneous equilibria involving a pure liquid or a pure solid, as the molar concentration of a pure solid or liquid is constant (i.e., independent of the amount present). In other words if a substance 'X' is involved, then [X(s)] and [X(l)] are constant, whatever the amount of 'X' is taken. Contrary to this, [X(g)] and [X(aq)] will Rationalised 2023-24 180 chemistry vary as the amount of X in a given volume varies. Let us take thermal dissociation of calcium carbonate which is an interesting and important example of heterogeneous chemical equilibrium. $CaCO_3 (s)$ $CaO (s)$ + $CO_2 (g)$ (6.16) On the basis of the stoichiometric equation, we can write, $K_c$ $\frac{[CaO(s)][CO_2(g)]}{[CaCO_3(s)]}$ Since [$CaCO_3(s)$] and [$CaO(s)$] are both constant, therefore modified equilibrium constant for the thermal decomposition of calcium carbonate will be $K´_c$ = [$CO_2(g)$] (6.17) or $K_p$ = $p_{CO_2}$ (6.18) This shows that at a particular temperature, there is a constant concentration or pressure of $CO_2$ in equilibrium with CaO(s) and $CaCO_3(s)$. Experimentally it has been found that at 1100 K, the pressure of $CO_2$ in equilibrium with $CaCO_3(s)$ and CaO(s), is 2.0 ×105 Pa. Therefore, equilibrium constant at 1100K for the above reaction is: $K_p$ = $P_{CO_2}$ = 2 × 105 Pa/105 Pa = 2.00 Similarly, in the equilibrium between nickel, carbon monoxide and nickel carbonyl (used in the purification of nickel), Ni (s) + 4 CO (g) $Ni(CO)_4 (g)$, the equilibrium constant is written as $K_c$ $\frac{[Ni(CO)_4]}{[CO]^4}$ It must be remembered that for the existence of heterogeneous equilibrium pure solids or liquids must also be present (however small the amount may be) at equilibrium, but their concentrations or partial pressures do not appear in the expression of the equilibrium constant. In the reaction, $Ag_2O(s)$ + $2HNO_3(aq)$ $2AgNO_3(aq)$ +$H_2O(l)$ $K_c$ = $\frac{[AgNO_3]^2}{[HNO_3]^2}$ **Units of Equilibrium Constant** The value of equilibrium constant $K_c$ can be calculated by substituting the concentration terms in mol/L and for $K_p$ partial pressure is substituted in Pa, kPa, bar or atm. This results in units of equilibrium constant based on molarity or pressure, unless the exponents of both the numerator and denominator are same. For the reactions, $H_2(g)$ + $I_2(g)$ 2HI, $K_c$ and $K_p$ have no unit. $N_2O_4(g)$ $2NO_2 (g)$, $K_c$ has unit mol/L and $K_p$ has unit bar Equilibrium constants can also be expressed as dimensionless quantities if the standard state of reactants and products are specified. For a pure gas, the standard state is 1bar. Therefore a pressure of 4 bar in standard state can be expressed as 4 bar/1 bar = 4, which is a dimensionless number. Standard state ($c^0$) for a solute is 1 molar solution and all concentrations can be measured with respect to it. The numerical value of equilibrium constant depends on the standard state chosen. Thus, in this system both $K_p$ and $K_c$ are dimensionless quantities but have different numerical values due to different standard states. **Problem 6.6** The value of $K_p$ for the reaction, $CO_2 (g)$ + C (s) 2CO (g) is 3.0 at 1000 K. If initially $P_{CO_2}$ = 0.48 bar and PCO = 0 bar and pure graphite is present, calculate the equilibrium partial pressures of CO and $CO_2$. **Solution** For the reaction, let 'x' be the decrease in pressure of $CO_2$, then $CO_2(g)$ + C(s) 2CO(g) Initial pressure: 0.48 bar 0 Rationalised 2023-24 EQUILIBRIUM 181 At equilibrium: (0.48 − x)bar 2x bar $K_p$ = $\frac{p_{CO}^2}{p_{CO_2}}$ $K_p$ = (2x)²/(0.48 − x) = 3 4x² = 3(0.48 − x) 4x² = 1.44 − x 4x² + 3x −

$1.44 = 0$ a = 4, b = 3, c = $-1.44$ x b b ac a ⬚- ⬚ - ⬚ 2 4 2 = $[-3 \pm \sqrt{(3)^2 - 4(4)(-1.44)}]/2 \times 4$ = $(-3 \pm 5.66)/8$ = $(-3 + 5.66)/8$ (as value of x cannot be negative hence we neglect that value) x = 2.66/8 = 0.33 The equilibrium partial pressures are, $pCO_2 = 2x = 2 \times 0.33 = 0.66$ bar $pCO_2 = 0.48 - x = 0.48 - 0.33 = 0.15$ bar 5. The equilibrium constant K for a reaction is related to the equilibrium constant of the corresponding reaction, whose equation is obtained by multiplying or dividing the equation for the original reaction by a small integer. Let us consider applications of equilibrium constant to: • predict the extent of a reaction on the basis of its magnitude, • predict the direction of the reaction, and • calculate equilibrium concentrations. 6.6.1 Predicting the Extent of a Reaction The numerical value of the equilibrium constant for a reaction indicates the extent of the reaction. But it is important to note that an equilibrium constant does not give any information about the rate at which the equilibrium is reached. The magnitude of Kc or Kp is directly proportional to the concentrations of products (as these appear in the numerator of equilibrium constant expression) and inversely proportional to the concentrations of the reactants (these appear in the denominator). This implies that a high value of K is suggestive of a high concentration of products and vice-versa. We can make the following generalisations concerning the composition of equilibrium mixtures: • If Kc > $10^3$, products predominate over reactants, i.e., if Kc is very large, the reaction proceeds nearly to completion. Consider the following examples: (a) The reaction of $H_2$ with $O_2$ at 500 K has a very large equilibrium constant, Kc = $2.4 \times 10^{47}$. (b) $H_2(g)$ + $Cl_2(g)$ 2HCl(g) at 300K has Kc = $4.0 \times 10^{31}$. (c) $H_2(g)$ + $Br_2(g)$ 2HBr (g) at 300 K, Kc = $5.4 \times 10^{18}$ • If Kc < $10^{-3}$, reactants predominate over products, i.e., if Kc is very small, the reaction proceeds rarely. Consider the following examples: 6.6 APPLICATIONS OF EQUILIBRIUM CONSTANTS Before considering the applications of equilibrium constants, let us summarise the important features of equilibrium constants as follows: 1. Expression for equilibrium constant is applicable only when concentrations of the reactants and products have attained constant value at equilibrium state. 2. The value of equilibrium constant is independent of initial concentrations of the reactants and products. 3. Equilibrium constant is temperature dependent having one unique value for a particular reaction represented by a balanced equation at a given temperature. 4. The equilibrium constant for the reverse reaction is equal to the inverse of the equilibrium constant for the forward reaction. Rationalised 2023-24 182 chemistry (a) The decomposition of $H_2O$ into $H_2$ and $O_2$ at 500 K has a very small equilibrium constant, Kc = $4.1 \times 10^{-48}$ (b) $N_2(g)$ + $O_2(g)$ 2NO(g), at 298 K has Kc = $4.8 \times 10^{-31}$. • If Kc is in the range of $10^{-3}$ to $10^3$, appreciable concentrations of both reactants and products are present. Consider the following examples: (a) For reaction of $H_2$ with $I_2$ to give HI, Kc = 57.0 at 700K. (b) Also, gas phase decomposition of $N_2O_4$ to $NO_2$ is another reaction with a value of Kc = $4.64 \times 10^{-3}$ at 25°C which is neither too small nor too large. Hence, equilibrium mixtures contain appreciable concentrations of both $N_2O_4$ and $NO_2$. These generarlisations are illustrated in Fig. 6.6 If Qc = Kc , the reaction mixture is already at equilibrium. Consider the gaseous reaction of $H_2$ with $I_2$, $H_2(g)$ + $I_2(g)$ 2HI(g); Kc = 57.0 at 700 K. Suppose we have molar concentrations $[H_2]_t$ =0.10M, $[I_2]_t$ = 0.20 M and $[HI]_t$ = 0.40 M. (the subscript t on the concentration symbols means that the concentrations were measured at some arbitrary time t, not necessarily at equilibrium). Thus, the reaction quotient, Qc at this stage of the reaction is given by, Qc = $[HI]_t^2$ / $[H_2]_t [I_2]_t$ = $(0.40)^2$/ $(0.10) \times (0.20)$ = 8.0 Now, in this case, Qc (8.0) does not equal Kc (57.0), so the mixture of $H_2(g)$, $I_2(g)$ and HI(g) is not at equilibrium; that is, more $H_2(g)$ and $I_2(g)$ will react to form more HI(g) and their concentrations will decrease till Qc = Kc . The reaction quotient, Qc is useful in predicting the direction of reaction by comparing the values of Qc and Kc . Thus, we can make the following generalisations concerning the direction of Fig.6.6 Dependence of extent of reaction on K the reaction (Fig. 6.7) : c 6.6.2 Predicting the Direction of the Reaction The equilibrium constant helps in predicting the direction in which a given reaction will proceed at any stage. For this purpose, we calculate the reaction quotient Q. The reaction quotient, Q (Qc with molar concentrations and QP with partial pressures) is defined in the same way as the

equilibrium constant $K_c$ except that the concentrations in $Q_c$ are not necessarily equilibrium values. For a general reaction: $a\ A + b\ B \rightleftharpoons c\ C + d\ D$ (6.19) $Q_c = [C]^c [D]^d / [A]^a[B]^b$ (6.20) Then, If $Q_c > K_c$, the reaction will proceed in the direction of reactants (reverse reaction). If $Q_c < K_c$, the reaction will proceed in the direction of the products (forward reaction). Fig. 6.7 Predicting the direction of the reaction • If $Q_c < K_c$, net reaction goes from left to right • If $Q_c > K_c$, net reaction goes from right to left. • If $Q_c = K_c$, no net reaction occurs. Problem 6.7 The value of $K_c$ for the reaction $2A \rightleftharpoons B + C$ is $2 \times 10^{-3}$. At a given time, the composition of reaction mixture is $[A] = [B] = [C] = 3 \times 10^{-4}$ M. In which direction the reaction will proceed?

The total pressure at equlibrium was found to be 9.15 bar. Calculate $K_c$, $K_p$ and partial pressure at equilibrium. Solution We know $pV = nRT$ Total volume ($V$) = 1 L Molecular mass of $N_2O_4$ = 92 g Number of moles = 13.8g/92 g = 0.15 of the gas (n) Gas constant (R) = 0.083 bar L mol$^{-1}$K$^{-1}$ Temperature (T) = 400 K $pV = nRT$ $p \times 1L = 0.15$ mol $\times 0.083$ bar L mol$^{-1}$K$^{-1} \times 400$ K $p = 4.98$ bar $N_2O_4 \rightleftharpoons 2NO_2$ Initial pressure: 4.98 bar 0 At equilibrium: (4.98 – x) bar 2x bar Hence, $p_{total}$ at equilibrium = $p_{N_2O_4} + p_{NO_2}$ 9.15 = (4.98 – x) + 2x 9.15 = 4.98 + x x = 9.15 – 4.98 = 4.17 bar Partial pressures at equilibrium are, $p_{N_2O_4}$ = 4.98 – 4.17 = 0.81 bar $p_{NO_2}$ = 2x = 2 × 4.17 = 8.34 bar $K_p = p_{NO_2}^2 / p_{N_2O_4} = (8.34)^2/0.81 = 85.87$ $K_p = K_c (RT)^{\Delta n}$ 85.87 = $K_c (0.083 \times 400)^1$ $K_c = 2.586 = 2.6$ Problem 6.9 3.00 mol of $PCl_5$ kept in 1L closed reaction vessel was allowed to attain equilibrium at 380K. Calculate composition of the mixture at equilibrium. $K_c = 1.80$ Solution $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ Initial concentration: 3.0 0 0 Solution For the reaction the reaction quotient $Q_c$ is given by, $Q_c = [B][C]/ [A]^2$ as $[A] = [B] = [C] = 3 \times 10^{-4}$M $Q_c = (3 \times 10^{-4})(3 \times 10^{-4}) / (3 \times 10^{-4})^2 = 1$ as $Q_c > K_c$ so the reaction will proceed in the reverse direction. 6.6.3 Calculating Equilibrium Concentrations In case of a problem in which we know the initial concentrations but do not know any of the equilibrium concentrations, the following three steps shall be followed: Step 1. Write the balanced equation for the reaction. Step 2. Under the balanced equation, make a table that lists for each substance involved in the reaction: (a) the initial concentration, (b) the change in concentration on going to equilibrium, and (c) the equilibrium concentration. In constructing the table, define x as the concentration (mol/L) of one of the substances that reacts on going to equilibrium, then use the stoichiometry of the reaction to determine the concentrations of the other substances in terms of x. Step 3. Substitute the equilibrium concentrations into the equilibrium equation for the reaction and solve for x. If you are to solve a quadratic equation choose the mathematical solution that makes chemical sense. Step 4. Calculate the equilibrium concentrations from the calculated value of x. Step 5. Check your results by substituting them into the equilibrium equation. Problem 6.8 13.8g of $N_2O_4$ was placed in a 1L reaction vessel at 400K and allowed to attain equilibrium $N_2O_4$ (g) $\rightleftharpoons$ 2NO$_2$ (g)

Let x mol per litre of $PCl_5$ be dissociated, At equilibrium: (3-x) x x $K_c = [PCl_3][Cl_2]/[PCl_5]$ $1.8 = x^2/ (3 - x)$ $x^2 + 1.8x - 5.4 = 0$ $x = [-1.8 \pm \sqrt{(1.8)^2 - 4(-5.4)}]/2$ $x = [-1.8 \pm \sqrt{3.24 + 21.6}]/2$ $x = [-1.8 \pm 4.98]/2$ $x = [-1.8 + 4.98]/2 = 1.59$ $[PCl_5] = 3.0 - x = 3 - 1.59 = 1.41$ M $[PCl_3] = [Cl_2] = x = 1.59$ M Taking antilog of both sides, we get, $K = e^{-\Delta G^0/RT}$ (6.23) Hence, using the equation (6.23), the reaction spontaneity can be interpreted in terms of the value of $\Delta G^0$. • If $\Delta G^0 < 0$, then $-\Delta G^0/RT$ is positive, and $e^{-\Delta G^0/RT} > 1$, making K >1, which implies a spontaneous reaction or the reaction which proceeds in the forward direction to such an extent that the products are present predominantly. • If $\Delta G^0 > 0$, then $-\Delta G^0/RT$ is negative, and $e^{-\Delta G^0/RT} < 1$, which implies a non-spontaneous reaction or a reaction which proceeds in the forward direction to such a small degree that only a very minute quantity of product is formed. Problem 6.10 The value of $\Delta G^0$ for the phosphorylation of glucose in glycolysis is 13.8 kJ/mol. Find the value of $K_c$ at 298 K. Solution $\Delta G^0$ = 13.8 kJ/mol = $13.8 \times 10^3$J/mol Also, $\Delta G^0 = -RT \ln K_c$ Hence, $\ln K_c = -13.8 \times 10^3$J/mol (8.314 J mol$^{-1}$K$^{-1} \times 298$ K) $\ln K_c = -5.569$ $K_c = e^{-5.569}$ $K_c = 3.81 \times 10^{-3}$ Problem 6.11 Hydrolysis of sucrose gives, Sucrose + $H_2O \rightleftharpoons$ Glucose + Fructose Equilibrium constant $K_c$ for the reaction is $2 \times 10^{13}$ at 300K.

Calculate $\Delta G^0$ at 300K. Solution $\Delta G^0 = - RT \ln Kc$ $\Delta G^0 = - 8.314 J \, mol^{-1}K^{-1} \times 300K \times \ln(2 \times 10^{13})$ $\Delta G^0 = - 7.64 \times 10^4 \, J \, mol^{-1}$ 6.8 FACTORS AFFECTING EQUILIBRIA One of the principal goals of chemical synthesis is to maximise the conversion of the 6.7 Relationship between Equilibrium Constant K, Reaction Quotient Q and Gibbs Energy G The value of Kc for a reaction does not depend on the rate of the reaction. However, as you have studied in Unit 5, it is directly related to the thermodynamics of the reaction and in particular, to the change in Gibbs energy, $\Delta G$. If, • $\Delta G$ is negative, then the reaction is spontaneous and proceeds in the forward direction. • $\Delta G$ is positive, then reaction is considered non-spontaneous. Instead, as reverse reaction would have a negative $\Delta G$, the products of the forward reaction shall be converted to the reactants. • $\Delta G$ is 0, reaction has achieved equilibrium; at this point, there is no longer any free energy left to drive the reaction. A mathematical expression of this thermodynamic view of equilibrium can be described by the following equation: $\Delta G = \Delta G^0 + RT \ln Q$ (6.21) where, $G^0$ is standard Gibbs energy. At equilibrium, when $\Delta G = 0$ and $Q = Kc$, the equation (6.21) becomes, $\Delta G = \Delta G^0 + RT \ln K = 0$ $\Delta G^0 = - RT \ln K$ (6.22) $\ln K = - \Delta G^0 / RT$ Rationalised 2023-24 EQUILIBRIUM 185 Fig. 6.8 Effect of addition of H2 on change of concentration for the reactants and products in the reaction, H2(g) + I2 (g) 2HI(g) reactants to products while minimising the expenditure of energy. This implies maximum yield of products at mild temperature and pressure conditions. If it does not happen, then the experimental conditions need to be adjusted. For example, in the Haber process for the synthesis of ammonia from N2 and H2, the choice of experimental conditions is of real economic importance. Annual world production of ammonia is about hundred million tones, primarily for use as fertilisers. Equilibrium constant, Kc is independent of initial concentrations. But if a system at equilibrium is subjected to a change in the concentration of one or more of the reacting substances, then the system is no longer at equilibrium; and net reaction takes place in some direction until the system returns to equilibrium once again. Similarly, a change in temperature or pressure of the system may also alter the equilibrium. In order to decide what course the reaction adopts and make a qualitative prediction about the effect of a change in conditions on equilibrium we use Le Chatelier's principle. It states that a change in any of the factors that determine the equilibrium conditions of a system will cause the system to change in such a manner so as to reduce or to counteract the effect of the change. This is applicable to all physical and chemical equilibria. We shall now be discussing factors which can influence the equilibrium. 6.8.1 Effect of Concentration Change In general, when equilibrium is disturbed by the addition/removal of any reactant/ products, Le Chatelier's principle predicts that: • The concentration stress of an added reactant/product is relieved by net reaction in the direction that consumes the added substance. • The concentration stress of a removed reactant/product is relieved by net reaction in the direction that replenishes the removed substance. or in other words, "When the concentration of any of the reactants or products in a reaction at equilibrium is changed, the composition of the equilibrium mixture changes so as to minimize the effect of concentration changes". Let us take the reaction, H2(g) + I2(g) 2HI(g) If H2 is added to the reaction mixture at equilibrium, then the equilibrium of the reaction is disturbed. In order to restore it, the reaction proceeds in a direction wherein H2 is consumed, i.e., more of H2 and I2 react to form HI and finally the equilibrium shifts in right (forward) direction (Fig.6.8). This is in accordance with the Le Chatelier's principle which implies that in case of addition of a reactant/product, a new equilibrium will be set up in which the concentration of the reactant/product should be less than what it was after the addition but more than what it was in the original mixture. The same point can be explained in terms of the reaction quotient, $Qc$, $Qc = [HI]^2/ [H2][I2]$ Rationalised 2023-24 186 chemistry Addition of hydrogen at equilibrium results in value of $Qc$ being less than Kc . Thus, in order to attain equilibrium again reaction moves in the forward direction. Similarly, we can say that removal of a product also boosts the forward reaction and increases the concentration of the products and this has great commercial application in cases of reactions, where the product is a gas

or a volatile substance. In case of manufacture of ammonia, ammonia is liquified and removed from the reaction mixture so that reaction keeps moving in forward direction. Similarly, in the large scale production of CaO (used as important building material) from CaCO3, constant removal of CO2 from the kiln drives the reaction to completion. It should be remembered that continuous removal of a product maintains Qc at a value less than Kc and reaction continues to move in the forward direction.

Effect of Concentration – An experiment This can be demonstrated by the following reaction: Fe3+(aq)+ SCN– (aq) [Fe(SCN)]2+(aq) (6.24) yellow colourless deep red (6.25) A reddish colour appears on adding two drops of 0.002 M potassium thiocynate solution to 1 mL of 0.2 M iron(III) nitrate solution due to the formation of [Fe(SCN)]2+. The intensity of the red colour becomes constant on attaining equilibrium. This equilibrium can be shifted in either forward or reverse directions depending on our choice of adding a reactant or a product. The equilibrium can be shifted in the opposite direction by adding reagents that remove Fe3+ or SCN– ions. For example, oxalic acid (H2C2O4), reacts with Fe3+ ions to form the stable complex ion [Fe(C2O4) 3] 3–, thus decreasing the concentration of free Fe3+(aq). In accordance with the Le Chatelier's principle, the concentration stress of removed Fe3+ is relieved by dissociation of [Fe(SCN)]2+ to replenish the Fe3+ ions. Because the concentration of [Fe(SCN)]2+ decreases, the intensity of red colour decreases. Addition of aq. HgCl2 also decreases red colour because Hg2+ reacts with SCN– ions to form stable complex ion [Hg(SCN)4] 2–. Removal of free SCN– (aq) shifts the equilibrium in equation (6.24) from right to left to replenish SCN– ions. Addition of potassium thiocyanate on the other hand increases the colour intensity of the solution as it shift the equilibrium to right. 6.8.2 Effect of Pressure Change A pressure change obtained by changing the volume can affect the yield of products in case of a gaseous reaction where the total number of moles of gaseous reactants and total number of moles of gaseous products are different. In applying Le Chatelier's principle to a heterogeneous equilibrium the effect of pressure changes on solids and liquids can be ignored because the volume (and concentration) of a solution/liquid is nearly independent of pressure. Consider the reaction, CO(g) + 3H2(g) CH4(g) + H2O(g) Here, 4 mol of gaseous reactants (CO + 3H2) become 2 mol of gaseous products (CH4 + H2O). Suppose equilibrium mixture (for above reaction) kept in a cylinder fitted with a piston at constant temperature is compressed to one half of its original volume. Then, total pressure will be doubled (according to pV = constant). The partial pressure and therefore, concentration of reactants and products have changed and the mixture is no longer at equilibrium. The direction in which the reaction goes to re-establish equilibrium can be predicted by applying the Le Chatelier's principle. Since pressure has doubled, the equilibrium now shifts in the forward direction, a direction in which the number of moles of the gas or pressure decreases (we know pressure is proportional to moles of the gas). This can also be understood by using reaction quotient, Qc . Let [CO], [H2], [CH4] and [H2O] be the molar concentrations at equilibrium for methanation reaction. When volume of the reaction mixture is halved, the Rationalised 2023-24 EQUILIBRIUM 187 Fig. 6.9 Effect of temperature on equilibrium for the reaction, 2NO2 (g) N2O4 (g) partial pressure and the concentration are doubled. We obtain the reaction quotient by replacing each equilibrium concentration by double its value. Qc = ▢ ( ) ▢▢▢▢ ( ) ▢▢▢▢ ( ) ▢▢▢▢ ( ) ▢▢▢ CH g H O g CO g H g 4 2 2 3 As Qc < Kc , the reaction proceeds in the forward direction. In reaction C(s) + CO2(g) 2CO(g), when pressure is increased, the reaction goes in the reverse direction because the number of moles of gas increases in the forward direction. 6.8.3 Effect of Inert Gas Addition If the volume is kept constant and an inert gas such as argon is added which does not take part in the reaction, the equilibrium remains undisturbed. It is because the addition of an inert gas at constant volume does not change the partial pressures or the molar concentrations of the substance involved in the reaction. The reaction quotient changes only if the added gas is a reactant or product involved in the reaction. 6.8.4 Effect of Temperature Change Whenever an equilibrium is disturbed by a change in the concentration, pressure or volume, the composition of the equilibrium mixture changes because

the reaction quotient, $Q_c$ no longer equals the equilibrium constant, $K_c$. However, when a change in temperature occurs, the value of equilibrium constant, $K_c$ is changed. In general, the temperature dependence of the equilibrium constant depends on the sign of $\Delta H$ for the reaction. • The equilibrium constant for an exothermic reaction (negative $\Delta H$) decreases as the temperature increases. • The equilibrium constant for an endothermic reaction (positive $\Delta H$) increases as the temperature increases. Temperature changes affect the equilibrium constant and rates of reactions. Production of ammonia according to the reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$; $\Delta H= -92.38$ kJ mol$^{-1}$ is an exothermic process. According to Le Chatelier's principle, raising the temperature shifts the equilibrium to left and decreases the equilibrium concentration of ammonia. In other words, low temperature is favourable for high yield of ammonia, but practically very low temperatures slow down the reaction and thus a catalyst is used. Effect of Temperature – An experiment Effect of temperature on equilibrium can be demonstrated by taking $NO_2$ gas (brown in colour) which dimerises into $N_2O_4$ gas (colourless). $2NO_2(g) \rightleftharpoons N_2O_4(g)$; $\Delta H = -57.2$ kJ mol$^{-1}$ $NO_2$ gas prepared by addition of Cu turnings to conc. $HNO_3$ is collected in two 5 mL test tubes (ensuring same intensity of colour of gas in each tube) and stopper sealed with araldite. Three 250 mL beakers 1, 2 and 3 containing freesing mixture, water at room temperature and hot water (363K), respectively, are taken (Fig. 6.9). Both the test tubes are placed in beaker 2 for 8-10 minutes. After this one is placed in beaker 1 and the other in beaker 3. The effect of temperature on direction of reaction is depicted very well in this experiment. At low temperatures in beaker 1, the forward reaction of formation of $N_2O_4$ is preferred, as reaction is exothermic, and thus, intensity of brown colour due to $NO_2$ decreases. While in beaker 3, high temperature favours the reverse reaction of Rationalised 2023-24 188 chemistry formation of $NO_2$ and thus, the brown colour intensifies. Effect of temperature can also be seen in an endothermic reaction, $[Co(H_2O)_6]^{3+}(aq) + 4Cl^-(aq) \rightleftharpoons [CoCl_4]^{2-}(aq) + 6H_2O(l)$ pink colourless blue At room temperature, the equilibrium mixture is blue due to $[CoCl_4]^{2-}$. When cooled in a freesing mixture, the colour of the mixture turns pink due to $[Co(H_2O)_6]^{3+}$. 6.8.5 Effect of a Catalyst A catalyst increases the rate of the chemical reaction by making available a new low energy pathway for the conversion of reactants to products. It increases the rate of forward and reverse reactions that pass through the same transition state and does not affect equilibrium. Catalyst lowers the activation energy for the forward and reverse reactions by exactly the same amount. Catalyst does not affect the equilibrium composition of a reaction mixture. It does not appear in the balanced chemical equation or in the equilibrium constant expression. Let us consider the formation of $NH_3$ from dinitrogen and dihydrogen which is highly exothermic reaction and proceeds with decrease in total number of moles formed as compared to the reactants. Equilibrium constant decreases with increase in temperature. At low temperature rate decreases and it takes long time to reach at equilibrium, whereas high temperatures give satisfactory rates but poor yields. German chemist, Fritz Haber discovered that a catalyst consisting of iron catalyse the reaction to occur at a satisfactory rate at temperatures, where the equilibrium concentration of $NH_3$ is reasonably favourable. Since the number of moles formed in the reaction is less than those of reactants, the yield of $NH_3$ can be improved by increasing the pressure. Optimum conditions of temperature and pressure for the synthesis of $NH_3$ using catalyst are around 500°C and 200 atm. Similarly, in manufacture of sulphuric acid by contact process, $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$; $K_c = 1.7 \times 10^{26}$ though the value of K is suggestive of reaction going to completion, but practically the oxidation of $SO_2$ to $SO_3$ is very slow. Thus, platinum or divanadium penta-oxide ($V_2O_5$) is used as catalyst to increase the rate of the reaction. Note: If a reaction has an exceedingly small K, a catalyst would be of little help. 6.9 IONIC EQUILIBRIUM IN SOLUTION Under the effect of change of concentration on the direction of equilibrium, you have incidently come across with the following equilibrium which involves ions: $Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons [Fe(SCN)]^{2+}(aq)$ There are numerous equilibria that involve ions only. In the following sections we will study the equilibria involving ions. It is well known that the

aqueous solution of sugar does not conduct electricity. However, when common salt (sodium chloride) is added to water it conducts electricity. Also, the conductance of electricity increases with an increase in concentration of common salt. Michael Faraday classified the substances into two categories based on their ability to conduct electricity. One category of substances conduct electricity in their aqueous solutions and are called electrolytes while the other do not and are thus, referred to as non-electrolytes. Faraday further classified electrolytes into strong and weak electrolytes. Strong electrolytes on dissolution in water are ionized almost completely, while the weak electrolytes are only partially dissociated. For example, an aqueous solution of sodium chloride is comprised entirely of sodium ions and chloride ions, while that of acetic acid mainly contains unionized acetic acid molecules and only some acetate ions and hydronium ions. This is because there is almost 100% ionization in case of sodium chloride as compared to less than 5% ionization of acetic acid which is a weak electrolyte. It should be noted Rationalised 2023-24 EQUILIBRIUM 189 Fig.6.10 Dissolution of sodium chloride in water. $Na^+$ and $Cl^-$ ions are stablised by their hydration with polar water molecules. that in weak electrolytes, equilibrium is established between ions and the unionized molecules. This type of equilibrium involving ions in aqueous solution is called ionic equilibrium. Acids, bases and salts come under the category of electrolytes and may act as either strong or weak electrolytes. 6.10 ACIDS, BASES AND SALTS Acids, bases and salts find widespread occurrence in nature. Hydrochloric acid present in the gastric juice is secreted by the lining of our stomach in a significant amount of 1.2-1.5 L/day and is essential for digestive processes. Acetic acid is known to be the main constituent of vinegar. Lemon and orange juices contain citric and ascorbic acids, and tartaric acid is found in tamarind paste. As most of the acids taste sour, the word "acid" has been derived from a latin word "acidus" meaning sour. Acids are known to turn blue litmus paper into red and liberate dihydrogen on reacting with some metals. Similarly, bases are known to turn red litmus paper blue, taste bitter and feel soapy. A common example of a base is washing soda used for washing purposes. When acids and bases are mixed in the right proportion they react with each other to give salts. Some commonly known examples of salts are sodium chloride, barium sulphate, sodium nitrate. Sodium chloride (common salt) is an important component of our diet and is formed by reaction between hydrochloric acid and sodium hydroxide. It exists in solid state as a cluster of positively charged sodium ions and negatively charged chloride ions which are held together due to electrostatic interactions between oppositely charged species (Fig.6.10). The electrostatic forces between two charges are inversely proportional to dielectric constant of the medium. Water, a universal solvent, possesses a very high dielectric constant of 80. Thus, when sodium chloride is dissolved in water, the electrostatic interactions are reduced by a factor of 80 and this facilitates the ions to move freely in the solution. Also, they are well-separated due to hydration with water molecules. Faraday was born near London into a family of very limited means. At the age of 14 he was an apprentice to a kind bookbinder who allowed Faraday to read the books he was binding. Through a fortunate chance he became laboratory assistant to Davy, and during 1813-4, Faraday accompanied him to the Continent. During this trip he gained much from the experience of coming into contact with many of the leading scientists of the time. In 1825, he succeeded Davy as Director of the Royal Institution laboratories, and in 1833 he also became the first Fullerian Professor of Chemistry. Faraday's first important work was on analytical chemistry. After 1821 much of his work was on electricity and magnetism and different electromagnetic phenomena. His ideas have led to the establishment of modern field theory. He discovered his two laws of electrolysis in 1834. Faraday was a very modest and kind hearted person. He declined all honours and avoided scientific controversies. He preferred to work alone and never had any assistant. He disseminated science in a variety of ways including his Friday evening discourses, which he founded at the Royal Institution. He has been very famous for his Christmas lecture on the 'Chemical History of a Candle'. He published nearly 450 scientific papers. Michael Faraday (1791–1867) Comparing, the ionization of hydrochloric

acid with that of acetic acid in water we find that though both of them are polar covalent

190 chemistry molecules, former is completely ionized into its constituent ions, while the latter is only partially ionized (< 5%). The extent to which ionization occurs depends upon the strength of the bond and the extent of solvation of ions produced. The terms dissociation and ionization have earlier been used with different meaning. Dissociation refers to the process of separation of ions in water already existing as such in the solid state of the solute, as in sodium chloride. On the other hand, ionization corresponds to a process in which a neutral molecule splits into charged ions in the solution. Here, we shall not distinguish between the two and use the two terms interchangeably. 6.10.1 Arrhenius Concept of Acids and Bases According to Arrhenius theory, acids are substances that dissociates in water to give hydrogen ions $H^+(aq)$ and bases are substances that produce hydroxyl ions $OH^-(aq)$. The ionization of an acid $HX(aq)$ can be represented by the following equations: $HX(aq) \rightarrow H^+(aq) + X^-(aq)$ or $HX(aq) + H_2O(l) \rightarrow H_3O^+(aq) + X^-(aq)$ A bare proton, $H^+$ is very reactive and cannot exist freely in aqueous solutions. Thus, it bonds to the oxygen atom of a solvent water molecule to give trigonal pyramidal hydronium ion, $H_3O^+$ {$[H(H_2O)]^+$} (see box). In this chapter we shall use $H^+(aq)$ and $H_3O^+(aq)$ interchangeably to mean the same i.e., a hydrated proton. Similarly, a base molecule like $MOH$ ionizes in aqueous solution according to the equation: $MOH(aq) \rightarrow M^+(aq) + OH^-(aq)$ The hydroxyl ion also exists in the hydrated form in the aqueous solution. Arrhenius concept of acid and base, however, suffers from the limitation of being applicable only to aqueous solutions and also, does not account for the basicity of substances like, ammonia which do not possess a hydroxyl group. 6.10.2 The Brönsted-Lowry Acids and Bases The Danish chemist, Johannes Brönsted and the English chemist, Thomas M. Lowry gave a more general definition of acids and bases. According to Brönsted-Lowry theory, acid is a substance that is capable of donating a hydrogen ion $H^+$ and bases are substances capable of accepting a hydrogen ion, $H^+$. In short, acids are proton donors and bases are proton acceptors. Consider the example of dissolution of $NH_3$ in $H_2O$ represented by the following equation: Hydronium and Hydroxyl Ions Hydrogen ion by itself is a bare proton with very small size (~$10^{-15}$ m radius) and intense electric field, binds itself with the water molecule at one of the two available lone pairs on it giving $H_3O^+$. This species has been detected in many compounds (e.g., $H_3O^+Cl^-$) in the solid state. In aqueous solution the hydronium ion is further hydrated to give species like $H_5O_2^+$, $H_7O_3^+$ and $H_9O_4^+$. Similarly the hydroxyl ion is hydrated to give several ionic species like $H_3O_2^-$, $H_5O_3^-$ and $H_7O_4^-$ etc. The basic solution is formed due to the presence of hydroxyl ions. In this reaction, water molecule acts as proton donor and ammonia molecule acts as proton acceptor and are thus, called Lowry-Brönsted acid and $H_9O_4^+$

EQUILIBRIUM 191 Arrhenius was born near Uppsala, Sweden. He presented his thesis, on the conductivities of electrolyte solutions, to the University of Uppsala in 1884. For the next five years he travelled extensively and visited a number of research centers in Europe. In 1895 he was appointed professor of physics at the newly formed University of Stockholm, serving its rector from 1897 to 1902. From 1905 until his death he was Director of physical chemistry at the Nobel Institute in Stockholm. He continued to work for many years on electrolytic solutions. In 1899 he discussed the temperature dependence of reaction rates on the basis of an equation, now usually known as Arrhenius equation. He worked in a variety of fields, and made important contributions to immunochemistry, cosmology, the origin of life, and the causes of ice age. He was the first to discuss the 'green house effect' calling by that name. He received Nobel Prize in Chemistry in 1903 for his theory of electrolytic dissociation and its use in the development of chemistry. base, respectively. In the reverse reaction, $H^+$ is transferred from $NH_4^+$ to $OH^-$. In this case, $NH_4^+$ acts as a Bronsted acid while $OH^-$ acted as a Brönsted base. The acid-base pair that differs only by one proton is called a conjugate acid-base pair. Therefore, $OH^-$ is called the conjugate base of an acid $H_2O$ and $NH_4^+$ is called conjugate acid of the base $NH_3$. If Brönsted acid is a strong acid then its conjugate base is a weak base and viceversa. It may be noted that conjugate acid has

one extra proton and each conjugate base has one less proton. Consider the example of ionization of hydrochloric acid in water. HCl(aq) acts as an acid by donating a proton to H2O molecule which acts as a base. in case of ammonia it acts as an acid by donating a proton. Problem 6.12 What will be the conjugate bases for the following Brönsted acids: HF, H2SO4 and HCO3 − ? Solution The conjugate bases should have one proton less in each case and therefore the corresponding conjugate bases are: F− , HSO4 − and CO3 2− respectively. Problem 6.13 Write the conjugate acids for the following Brönsted bases: NH2 − , NH3 and HCOO− . Solution The conjugate acid should have one extra proton in each case and therefore the corresponding conjugate acids are: NH3, NH4 + and HCOOH respectively. Problem 6.14 The species: H2O, HCO3 − , HSO4 − and NH3 can act both as Bronsted acids and bases. For each case give the corresponding conjugate acid and conjugate base. Solution The answer is given in the following Table: Species Conjugate Conjugate acid base H2O H3O+ OH− HCO3 − H2CO3 CO3 2− HSO4 − H2SO4 SO4 2− NH3 NH4 + NH2 − Svante Arrhenius (1859-1927) It can be seen in the above equation, that water acts as a base because it accepts the proton. The species H3O+ is produced when water accepts a proton from HCl. Therefore, Cl− is a conjugate base of HCl and HCl is the conjugate acid of base Cl − . Similarly, H2O is a conjugate base of an acid H3O+ and H3O+ is a conjugate acid of base H2O. It is interesting to observe the dual role of water as an acid and a base. In case of reaction with HCl water acts as a base while Rationalised 2023-24 192 chemistry 6.10.3 Lewis Acids and Bases G.N. Lewis in 1923 defined an acid as a species which accepts electron pair and base which donates an electron pair. As far as bases are concerned, there is not much difference between Brönsted-Lowry and Lewis concepts, as the base provides a lone pair in both the cases. However, in Lewis concept many acids do not have proton. A typical example is reaction of electron deficient species BF3 with NH3. BF3 does not have a proton but still acts as an acid and reacts with NH3 by accepting its lone pair of electrons. The reaction can be represented by, BF3 + :NH3 → BF3:NH3 Electron deficient species like AlCl3, Co3+, Mg2+, etc. can act as Lewis acids while species like H2O, NH3, OH− etc. which can donate a pair of electrons, can act as Lewis bases. Problem 6.15 Classify the following species into Lewis acids and Lewis bases and show how these act as such: (a) HO− (b) F− (c) H+ (d) BCl3 Solution (a) Hydroxyl ion is a Lewis base as it can donate an electron lone pair (:OH− ). (b) Flouride ion acts as a Lewis base as it can donate any one of its four electron lone pairs. (c) A proton is a Lewis acid as it can accept a lone pair of electrons from bases like hydroxyl ion and fluoride ion. (d) BCl3 acts as a Lewis acid as it can accept a lone pair of electrons from species like ammonia or amine molecules. 6.11 IONIZATION OF ACIDS AND BASES Arrhenius concept of acids and bases becomes useful in case of ionization of acids and bases as mostly ionizations in chemical and biological systems occur in aqueous medium. Strong acids like perchloric acid (HClO4), hydrochloric acid (HCl), hydrobromic acid (HBr), hyrdoiodic acid (HI), nitric acid (HNO3) and sulphuric acid (H2SO4) are termed strong because they are almost completely dissociated into their constituent ions in an aqueous medium, thereby acting as proton (H+) donors. Similarly, strong bases like lithium hydroxide (LiOH), sodium hydroxide (NaOH), potassium hydroxide (KOH), caesium hydroxide (CsOH) and barium hydroxide Ba(OH)2 are almost completely dissociated into ions in an aqueous medium giving hydroxyl ions, OH− . According to Arrhenius concept they are strong acids and bases as they are able to completely dissociate and produce H3O+ and OH− ions respectively in the medium. Alternatively, the strength of an acid or base may also be gauged in terms of Brönsted-Lowry concept of acids and bases, wherein a strong acid means a good proton donor and a strong base implies a good proton acceptor. Consider, the acid-base dissociation equilibrium of a weak acid HA, HA(aq) + H2O(l) H3O+(aq) + A− (aq) conjugate conjugate acid base acid base In section 6.10.2 we saw that acid (or base) dissociation equilibrium is dynamic involving a transfer of proton in forward and reverse directions. Now, the question arises that if the equilibrium is dynamic then with passage of time which direction is favoured? What is the driving force behind it? In order to answer these questions we shall deal into the issue of comparing the strengths of the two acids (or bases) involved

in the dissociation equilibrium. Consider the two acids HA and H3O+ present in the above mentioned acid-dissociation equilibrium. We have to see which amongst them is a stronger proton donor. Whichever exceeds in its tendency of donating a proton over the other shall be termed as the stronger acid and the equilibrium will shift in the direction of weaker acid. Say, if HA is a stronger acid than H3O+, then HA will donate protons and not H3O+, and the solution will mainly contain A– and H3O+ ions. The equilibrium moves in the direction of formation of weaker acid Rationalised 2023-24 EQUILIBRIUM 193 and weaker base because the stronger acid donates a proton to the stronger base. It follows that as a strong acid dissociates completely in water, the resulting base formed would be very weak i.e., strong acids have very weak conjugate bases. Strong acids like perchloric acid (HClO4), hydrochloric acid (HCl), hydrobromic acid (HBr), hydroiodic acid (HI), nitric acid (HNO3) and sulphuric acid (H2SO4) will give conjugate base ions ClO4 – , Cl, Br– , I– , NO3 – and HSO4 – , which are much weaker bases than H2O. Similarly a very strong base would give a very weak conjugate acid. On the other hand, a weak acid say HA is only partially dissociated in aqueous medium and thus, the solution mainly contains undissociated HA molecules. Typical weak acids are nitrous acid (HNO2), hydrofluoric acid (HF) and acetic acid (CH3COOH). It should be noted that the weak acids have very strong conjugate bases. For example, NH2 – , O2– and H– are very good proton acceptors and thus, much stronger bases than H2O. Certain water soluble organic compounds like phenolphthalein and bromothymol blue behave as weak acids and exhibit different colours in their acid (HIn) and conjugate base (In– ) forms. HIn(aq) + H2O(l) H3O+(aq) + In– (aq) acid conjugate conjugate indicator acid base colour A colour B Such compounds are useful as indicators in acid-base titrations, and finding out H+ ion concentration. 6.11.1 The Ionization Constant of Water and its Ionic Product Some substances like water are unique in their ability of acting both as an acid and a base. We have seen this in case of water in section 6.10.2. In presence of an acid, HA it accepts a proton and acts as the base while in the presence of a base, B– it acts as an acid by donating a proton. In pure water, one H2O molecule donates proton and acts as an acid and another water molecules accepts a proton and acts as a base at the same time. The following equilibrium exists: H2O(l) + H2O(l) H3O+(aq) + OH– (aq) acid base conjugate conjugate acid base The dissociation constant is represented by, K = [H3O+][OH– ] / [H2O] (6.26) The concentration of water is omitted from the denominator as water is a pure liquid and its concentration remains constant. [H2O] is incorporated within the equilibrium constant to give a new constant, Kw, which is called the ionic product of water. Kw = [H+][OH– ] (6.27) The concentration of H+ has been found out experimentally as 1.0 × 10–7 M at 298 K. And, as dissociation of water produces equal number of H+ and OH– ions, the concentration of hydroxyl ions, [OH– ] = [H+] = 1.0 × 10–7 M. Thus, the value of Kw at 298K, Kw = [H3O+][OH– ] = (1 × 10–7) 2 = 1 × 10–14 M2 (6.28) The value of Kw is temperature dependent as it is an equilibrium constant. The density of pure water is 1000 g / L and its molar mass is 18.0 g /mol. From this the molarity of pure water can be given as, [H2O] = (1000 g /L)(1 mol/18.0 g) = 55.55 M. Therefore, the ratio of dissociated water to that of undissociated water can be given as: 10–7 / (55.55) = 1.8 × 10–9 or ~ 2 in 10–9 (thus, equilibrium lies mainly towards undissociated water) We can distinguish acidic, neutral and basic aqueous solutions by the relative values of the H3O+ and OH– concentrations: Acidic: [H3O+] > [OH– ] Neutral: [H3O+] = [OH– ] Basic : [H3O+] < [OH– ] 6.11.2 The pH Scale Hydronium ion concentration in molarity is more conveniently expressed on a logarithmic scale known as the pH scale. The pH of a solution is defined as the negative logarithm to base 10 of the activity aH - ⬚ of hydrogen Rationalised 2023-24 194 chemistry ion. In dilute solutions (< 0.01 M), activity of hydrogen ion (H+) is equal in magnitude to molarity represented by [H+]. It should be noted that activity has no units and is defined as: = [H+] / mol L–1 From the definition of pH, the following can be written, pH = – log aH+ = – log {[H+] / mol L–1} Thus, an acidic solution of HCl (10–2 M) will have a pH = 2. Similarly, a basic solution of NaOH having [OH– ] =10–4 M and [H3O+] = 10–10 M will have a pH = 10. At 25 °C, pure water has a concentration of hydrogen ions, [H+] = 10–7 M. Hence, the pH of pure

water is given as: pH = –log(10–7) = 7 Acidic solutions possess a concentration of hydrogen ions, [H+] > 10–7 M, while basic solutions possess a concentration of hydrogen ions, [H+] < 10–7 M. thus, we can summarise that Acidic solution has pH < 7 Basic solution has pH > 7 Neutral solution has pH = 7 Now again, consider the equation (6.28) at 298 K Kw = [H3O+] [OH– ] = 10–14 Taking negative logarithm on both sides of equation, we obtain –log Kw = – log {[H3O+] [OH– ]} = – log [H3O+] – log [OH– ] = – log 10–14 pKw = pH + pOH = 14 (6.29) Note that although Kw may change with temperature the variations in pH with temperature are so small that we often ignore it. pKw is a very important quantity for aqueous solutions and controls the relative concentrations of hydrogen and hydroxyl ions as their product is a constant. It should be noted that as the pH scale is logarithmic, a change in pH by just one unit also means change in [H+] by a factor of 10. Similarly, when the hydrogen ion concentration, [H+] changes by a factor of 100, the value of pH changes by 2 units. Now you can realise why the change in pH with temperature is often ignored. Measurement of pH of a solution is very essential as its value should be known when dealing with biological and cosmetic applications. The pH of a solution can be found roughly with the help of pH paper that has different colour in solutions of different pH. Now-a-days pH paper is available with four strips on it. The different strips have different colours (Fig. 6.11) at the same pH. The pH in the range of 1-14 can be determined with an accuracy of ~0.5 using pH paper. Fig.6.11 pH-paper with four strips that may have different colours at the same pH For greater accuracy pH meters are used. pH meter is a device that measures the pH-dependent electrical potential of the test solution within 0.001 precision. pH meters of the size of a writing pen are now available in the market. The pH of some very common substances are given in Table 6.5 (page 195). Problem 6.16 The concentration of hydrogen ion in a sample of soft drink is $3.8 \times 10^{-3}$M. what is its pH ? Solution pH = – log[$3.8 \times 10^{-3}$] = – {log[3.8] + log[10–3]} = – {(0.58) + (– 3.0)} = – { – 2.42} = 2.42 Therefore, the pH of the soft drink is 2.42 and it can be inferred that it is acidic. Problem 6.17 Calculate pH of a $1.0 \times 10^{-8}$ M solution of HCl. Rationalised 2023-24 EQUILIBRIUM 195 Table 6.6 The Ionization Constants of Some Selected Weak Acids (at 298K) Acid Ionization Constant, Ka Hydrofluoric Acid (HF) $3.5 \times 10^{-4}$ Nitrous Acid (HNO2) $4.5 \times 10^{-4}$ Formic Acid (HCOOH) $1.8 \times 10^{-4}$ Niacin (C5H4NCOOH) $1.5 \times 10^{-5}$ Acetic Acid (CH3COOH) $1.74 \times 10^{-5}$ Benzoic Acid (C6H5COOH) $6.5 \times 10^{-5}$ Hypochlorous Acid (HCIO) $3.0 \times 10^{-8}$ Hydrocyanic Acid (HCN) $4.9 \times 10^{-10}$ Phenol (C6H5OH) $1.3 \times 10^{-10}$ Solution 2H2O (l) H3O+ (aq) + OH– (aq) Kw = [OH– ][H3O+] = 10–14 Let, x = [OH– ] = [H3O+] from H2O. The H3O+ concentration is generated (i) from the ionization of HCl dissolved i.e., HCl(aq) + H2O(l) H3O+ (aq) + Cl – (aq), and (ii) from ionization of H2O. In these very dilute solutions, both sources of H3O+ must be considered: [H3O+] = 10–8 + x Kw = (10–8 + x)(x) = 10–14 or x2 + 10–8 x – 10–14 = 0 [OH– ] = x = $9.5 \times 10^{-8}$ So, pOH = 7.02 and pH = 6.98 6.11.3 Ionization Constants of Weak Acids Consider a weak acid HX that is partially ionized in the aqueous solution. The equilibrium can be expressed by: HX(aq) + H2O(l) H3O+(aq) + X– (aq) Initial concentration (M) c 0 0 Let α be the extent of ionization Change (M) -cα +cα +cα Equilibrium concentration (M) c-cα cα cα Here, c = initial concentration of the undissociated acid, HX at time, t = 0. α = extent up to which HX is ionized into ions. Using these notations, we can derive the equilibrium constant for the above discussed acid-dissociation equilibrium: Ka = c2α2 / c(1-α) = cα2 / 1-α Ka is called the dissociation or ionization constant of acid HX. It can be represented alternatively in terms of molar concentration as follows, Ka = [H+][X– ] / [HX] (6.30) At a given temperature T, Ka is a measure of the strength of the acid HX i.e., larger the value of Ka, the stronger is the acid. Ka is a dimensionless quantity with the understanding that the standard state concentration of all species is 1M. The values of the ionization constants of some selected weak acids are given in Table 6.6. Table 6.5 The pH of Some Common Substances Name of the Fluid pH Name of the Fluid pH Saturated solution of NaOH ~15 Black Coffee 5.0 0.1 M NaOH solution 13 Tomato juice ~4.2 Lime water 10.5 Soft drinks and vinegar ~3.0 Milk of magnesia 10 Lemon juice ~2.2 Egg white, sea water 7.8 Gastric juice ~1.2 Human blood 7.4 1M HCl solution ~0 Milk 6.8 Concentrated HCl ~–1.0 Human Saliva 6.4

The pH scale for the hydrogen ion concentration has been so useful that besides pKw, it has been extended to other species and chemistry quantities. Thus, we have: $pK_a = -\log (K_a)$ (6.31) Knowing the ionization constant, $K_a$ of an acid and its initial concentration, c, it is possible to calculate the equilibrium concentration of all species and also the degree of ionization of the acid and the pH of the solution. A general step-wise approach can be adopted to evaluate the pH of the weak electrolyte as follows: Step 1. The species present before dissociation are identified as Brönsted-Lowry acids/bases. Step 2. Balanced equations for all possible reactions i.e., with a species acting both as acid as well as base are written. Step 3. The reaction with the higher $K_a$ is identified as the primary reaction whilst the other is a subsidiary reaction. Step 4. Enlist in a tabular form the following values for each of the species in the primary reaction (a) Initial concentration, c. (b) Change in concentration on proceeding to equilibrium in terms of α, degree of ionization. (c) Equilibrium concentration. Step 5. Substitute equilibrium concentrations into equilibrium constant equation for principal reaction and solve for α. Step 6. Calculate the concentration of species in principal reaction. Step 7. Calculate pH $= -\log[H_3O^+]$ The above mentioned methodology has been elucidated in the following examples. Solution The following proton transfer reactions are possible: 1) $HF + H_2O \rightleftharpoons H_3O^+ + F^-$ $K_a = 3.2 \times 10^{-4}$ 2) $H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$ $K_w = 1.0 \times 10^{-14}$ As $K_a \gg K_w$, [1] is the principle reaction. $HF + H_2O \rightleftharpoons H_3O^+ + F^-$ Initial concentration (M) 0.02 0 0 Change (M) $-0.02\alpha$ $+0.02\alpha$ $+0.02\alpha$ Equilibrium concentration (M) $0.02 - 0.02\alpha$ $0.02\alpha$ $0.02\alpha$ Substituting equilibrium concentrations in the equilibrium reaction for principal reaction gives: $K_a = (0.02\alpha)^2 / (0.02 - 0.02\alpha) = 0.02 \alpha^2 / (1 - \alpha) = 3.2 \times 10^{-4}$ We obtain the following quadratic equation: $\alpha^2 + 1.6 \times 10^{-2}\alpha - 1.6 \times 10^{-2} = 0$ The quadratic equation in α can be solved and the two values of the roots are: α = + 0.12 and − 0.12 The negative root is not acceptable and hence, α = 0.12 This means that the degree of ionization, α = 0.12, then equilibrium concentrations of other species viz., HF, F − and $H_3O^+$ are given by: $[H_3O^+] = [F^-] = c\alpha = 0.02 \times 0.12 = 2.4 \times 10^{-3}$ M $[HF] = c(1 - \alpha) = 0.02 (1 - 0.12) = 17.6 \times 10^{-3}$ M $pH = -\log[H^+] = -\log(2.4 \times 10^{-3}) = 2.62$ Problem 6.19 The pH of 0.1M monobasic acid is 4.50. Calculate the concentration of species $H^+$, $A^-$ Problem 6.18 The ionization constant of HF is $3.2 \times 10^{-4}$. Calculate the degree of dissociation of HF in its 0.02 M solution. Calculate the concentration of all species present ($H_3O^+$, $F^-$ and HF) in the solution and its pH. Table 6.7 The Values of the Ion izat ion Constant of Some Weak Bases at 298 K Base Kb Dimethylamine, $(CH_3)_2NH$ $5.4 \times 10^{-4}$ Triethylamine, $(C_2H_5)_3N$ $6.45 \times 10^{-5}$ Ammonia, $NH_3$ or $NH_4OH$ $1.77 \times 10^{-5}$ Quinine, (A plant product) $1.10 \times 10^{-6}$ Pyridine, $C_5H_5N$ $1.77 \times 10^{-9}$ Aniline, $C_6H_5NH_2$ $4.27 \times 10^{-10}$ Urea, $CO(NH_2)_2$ $1.3 \times 10^{-14}$ and HA at equilibrium. Also, determine the value of $K_a$ and $pK_a$ of the monobasic acid. Solution $pH = -\log[H^+]$ Therefore, $[H^+] = 10^{-pH} = 10^{-4.50} = 3.16 \times 10^{-5}$ $[H^+] = [A^-] = 3.16 \times 10^{-5}$ Thus, $K_a = [H^+][A^-] / [HA]$ $[HA]_{eqlbm} = 0.1 - (3.16 \times 10^{-5}) \otimes 0.1$ $K_a = (3.16 \times 10^{-5})^2 / 0.1 = 1.0 \times 10^{-8}$ $pK_a = -\log(10^{-8}) = 8$ Alternatively, "Percent dissociation" is another useful method for measure of strength of a weak acid and is given as: Percent dissociation $= [HA]_{dissociated}/[HA]_{initial} \times 100\%$ (6.32) Problem 6.20 Calculate the pH of 0.08M solution of hypochlorous acid, HOCl. The ionization constant of the acid is $2.5 \times 10^{-5}$. Determine the percent dissociation of HOCl. Solution $HOCl(aq) + H_2O (l) \rightleftharpoons H_3O^+(aq) + ClO^-(aq)$ Initial concentration (M) 0.08 0 0 Change to reach equilibrium concentration (M) $-x$ $+x$ $+x$ equilibrium concentartion (M) $0.08 - x$ x x $K_a = \{[H_3O^+][ClO^-] / [HOCl]\} = x^2 / (0.08 - x)$ As $x \ll 0.08$, therefore $0.08 - x \otimes 0.08$ $x^2 / 0.08 = 2.5 \times 10^{-5}$ $x^2 = 2.0 \times 10^{-6}$, thus, $x = 1.41 \times 10^{-3}$ $[H^+] = 1.41 \times 10^{-3}$ M. Therefore, Percent dissociation $= \{[HOCl]_{dissociated} / [HOCl]_{initial}\} \times 100 = 1.41 \times 10^{-3} \times 10^2 / 0.08 = 1.76$ %. $pH = -\log(1.41 \times 10^{-3}) = 2.85$. 6.11.4 Ionization of Weak Bases The ionization of base MOH can be represented by equation: $MOH(aq) \rightleftharpoons M^+(aq) + OH^-(aq)$ In a weak base there is partial ionization of MOH into $M^+$ and $OH^-$, the case is similar to that of acid-dissociation equilibrium. The equilibrium constant for base ionization is called base ionization constant and is represented by $K_b$. It can be expressed in terms of concentration in molarity of various species in equilibrium by the following equation: $K_b = [M^+][OH^-$

] / [MOH] (6.33) Alternatively, if c = initial concentration of base and $\alpha$ = degree of ionization of base i.e. the extent to which the base ionizes. When equilibrium is reached, the equilibrium constant can be written as: $K_b = (c\alpha)^2 / c(1-\alpha) = c\alpha^2 / (1-\alpha)$ The values of the ionization constants of some selected weak bases, $K_b$ are given in Table 6.7. Many organic compounds like amines are weak bases. Amines are derivatives of ammonia in which one or more hydrogen atoms are replaced by another group. For example, methylamine, codeine, quinine and Rationalised 2023-24 198 chemistry nicotine all behave as very weak bases due to their very small $K_b$. Ammonia produces $OH^-$ in aqueous solution: $NH_3(aq) + H_2O(l)$ $NH_4^+(aq) + OH^-(aq)$ The pH scale for the hydrogen ion concentration has been extended to get: $pK_b = -\log(K_b)$ (6.34) Problem 6.21 The pH of 0.004M hydrazine solution is 9.7. Calculate its ionization constant $K_b$ and $pK_b$. Solution $NH_2NH_2 + H_2O$ $NH_2NH_3^+ + OH^-$ From the pH we can calculate the hydrogen ion concentration. Knowing hydrogen ion concentration and the ionic product of water we can calculate the concentration of hydroxyl ions. Thus we have: $[H^+]$ = antilog $(-pH)$ = antilog $(-9.7) = 1.67 \times 10^{-10}$ $[OH^-] = K_w / [H^+] = 1 \times 10^{-14} / 1.67 \times 10^{-10} = 5.98 \times 10^{-5}$ The concentration of the corresponding hydrazinium ion is also the same as that of hydroxyl ion. The concentration of both these ions is very small so the concentration of the undissociated base can be taken equal to 0.004M. Thus, $K_b = [NH_2NH_3^+][OH^-] / [NH_2NH_2] = (5.98 \times 10^{-5})^2 / 0.004 = 8.96 \times 10^{-7}$ $pK_b = -\log K_b = -\log(8.96 \times 10^{-7}) = 6.04$. Problem 6.22 Calculate the pH of the solution in which 0.2M $NH_4Cl$ and 0.1M $NH_3$ are present. The $pK_b$ of ammonia solution is 4.75. Solution $NH_3 + H_2O$ $NH_4^+ + OH^-$ The ionization constant of $NH_3$, $K_b$ = antilog $(-pK_b)$ i.e. $K_b = 10^{-4.75} = 1.77 \times 10^{-5}$ M $NH_3 + H_2O$ $NH_4^+ + OH^-$ Initial concentration (M) 0.10 0.20 0 Change to reach equilibrium (M) $-x$ $+x$ $+x$ At equilibrium (M) $0.10 - x$ $0.20 + x$ $x$ $K_b = [NH_4^+][OH^-] / [NH_3] = (0.20 + x)(x) / (0.1 - x) = 1.77 \times 10^{-5}$ As $K_b$ is small, we can neglect x in comparison to 0.1M and 0.2M. Thus, $[OH^-] = x = 0.88 \times 10^{-5}$ Therefore, $[H^+] = 1.12 \times 10^{-9}$ $pH = -\log[H^+] = 8.95$. 6.11.5 Relation between $K_a$ and $K_b$ As seen earlier in this chapter, $K_a$ and $K_b$ represent the strength of an acid and a base, respectively. In case of a conjugate acid-base pair, they are related in a simple manner so that if one is known, the other can be deduced. Considering the example of $NH_4^+$ and $NH_3$ we see, $NH_4^+(aq) + H_2O(l)$ $H_3O^+(aq) + NH_3(aq)$ $K_a = [H_3O^+][NH_3] / [NH_4^+] = 5.6 \times 10^{-10}$ $NH_3(aq) + H_2O(l)$ $NH_4^+(aq) + OH^-(aq)$ $K_b = [NH_4^+][OH^-] / NH_3 = 1.8 \times 10^{-5}$ Net: $2 H_2O(l)$ $H_3O^+(aq) + OH^-(aq)$ $K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$ M Where, $K_a$ represents the strength of $NH_4^+$ as an acid and $K_b$ represents the strength of $NH_3$ as a base. It can be seen from the net reaction that the equilibrium constant is equal to the product of equilibrium constants $K_a$ and $K_b$ for the reactions added. Thus, $K_a \times K_b = \{[H_3O^+][NH_3] / [NH_4^+]\} \times \{[NH_4^+][OH^-] / [NH_3]\} = [H_3O^+][OH^-] = K_w = (5.6 \times 10^{-10}) \times (1.8 \times 10^{-5}) = 1.0 \times 10^{-14}$ M Rationalised 2023-24 EQUILIBRIUM 199 This can be extended to make a generalisation. The equilibrium constant for a net reaction obtained after adding two (or more) reactions equals the product of the equilibrium constants for individual reactions: $K_{NET} = K_1 \times K_2 \times \ldots\ldots$ (6.35) Similarly, in case of a conjugate acid-base pair, $K_a \times K_b = K_w$ (6.36) Knowing one, the other can be obtained. It should be noted that a strong acid will have a weak conjugate base and vice-versa. Alternatively, the above expression $K_w = K_a \times K_b$, can also be obtained by considering the base-dissociation equilibrium reaction: $B(aq) + H_2O(l)$ $BH^+(aq) + OH^-(aq)$ $K_b = [BH^+][OH^-] / [B]$ As the concentration of water remains constant it has been omitted from the denominator and incorporated within the dissociation constant. Then multiplying and dividing the above expression by $[H^+]$, we get: $K_b = [BH^+][OH^-][H^+] / [B][H^+] = \{[OH^-][H^+]\}\{[BH^+] / [B][H^+]\} = K_w / K_a$ or $K_a \times K_b = K_w$ It may be noted that if we take negative logarithm of both sides of the equation, then pK values of the conjugate acid and base are related to each other by the equation: $pK_a + pK_b = pK_w = 14$ (at 298K) Problem 6.23 Determine the degree of ionization and pH of a 0.05M of ammonia solution. The ionization constant of ammonia can be taken from Table 6.7. Also, calculate the ionization constant of the conjugate acid of ammonia. Solution The ionization of $NH_3$ in water is represented by equation: $NH_3 + H_2O$ $NH_4^+ + OH^-$ We use equation (6.33) to calculate hydroxyl ion concentration, $[OH^-] = c\alpha = 0.05\ \alpha$ $K_b = 0.05$

$\alpha^2 / (1 - \alpha)$ The value of $\alpha$ is small, therefore the quadratic equation can be simplified by neglecting $\alpha$ in comparison to 1 in the denominator on right hand side of the equation, Thus, $K_b = c\,\alpha^2$ or $\alpha = \sqrt{}$ $(1.77 \times 10^{-5} / 0.05) = 0.018$. $[OH^-] = c\,\alpha = 0.05 \times 0.018 = 9.4 \times 10^{-4}M$. $[H^+] = K_w / [OH^-] = 10^{-14} / (9.4 \times 10^{-4}) = 1.06 \times 10^{-11}$ $pH = -\log(1.06 \times 10^{-11}) = 10.97$. Now, using the relation for conjugate acid-base pair, $K_a \times K_b = K_w$ using the value of $K_b$ of $NH_3$ from Table 6.7. We can determine the concentration of conjugate acid $NH_4^+$ $K_a = K_w / K_b = 10^{-14} / 1.77 \times 10^{-5} = 5.64 \times 10^{-10}$. 6.11.6 Di- and Polybasic Acids and Diand Polyacidic Bases Some of the acids like oxalic acid, sulphuric acid and phosphoric acids have more than one ionizable proton per molecule of the acid. Such acids are known as polybasic or polyprotic acids. The ionization reactions for example for a dibasic acid $H_2X$ are represented by the equations: $H_2X(aq)$ $H^+(aq) + HX^-(aq)$ $HX^-(aq)$ $H^+(aq) + X^{2-}(aq)$ And the corresponding equilibrium constants are given below: $K_{a1} = \{[H^+][HX^-]\} / [H_2X]$ and Rationalised 2023-24 200 chemistry $K_{a2} = \{[H^+][X^{2-}]\} / [HX^-]$ Here, $K_{a1}$ and $K_{a2}$ are called the first and second ionization constants respectively of the acid $H_2X$. Similarly, for tribasic acids like $H_3PO_4$ we have three ionization constants. The values of the ionization constants for some common polyprotic acids are given in Table 6.8. In general, when strength of H-A bond decreases, that is, the energy required to break the bond decreases, HA becomes a stronger acid. Also, when the H-A bond becomes more polar i.e., the electronegativity difference between the atoms H and A increases and there is marked charge separation, cleavage of the bond becomes easier thereby increasing the acidity. But it should be noted that while comparing elements in the same group of the periodic table, H-A bond strength is a more important factor in determining acidity than its polar nature. As the size of A increases down the group, H-A bond strength decreases and so the acid strength increases. For example, Size increases HF << HCl << HBr << HI Acid strength increases Similarly, $H_2S$ is stronger acid than $H_2O$. But, when we discuss elements in the same row of the periodic table, H-A bond polarity becomes the deciding factor for determining the acid strength. As the electronegativity of A increases, the strength of the acid also increases. For example, Electronegativity of A increases $CH_4 < NH_3 < H_2O < HF$ Acid strength increases 6.11.8 Common Ion Effect in the Ionization of Acids and Bases Consider an example of acetic acid dissociation equilibrium represented as: $CH_3COOH(aq)$ $H^+(aq) + CH_3COO^-(aq)$ or $HAc(aq)$ $H^+(aq) + Ac^-(aq)$ $K_a = [H^+][Ac^-] / [HAc]$ Addition of acetate ions to an acetic acid solution results in decreasing the concentration of hydrogen ions, $[H^+]$. Also, if $H^+$ ions are added from an external source then the equilibrium moves in the direction of undissociated acetic acid i.e., in a direction of reducing the concentration of hydrogen ions, $[H^+]$. This phenomenon is an example Table 6.8 The Ionization Constants of Some Common Polyprotic Acids (298K) It can be seen that higher order ionization constants ($K_{a2}$, $K_{a3}$) are smaller than the lower order ionization constant ($K_{a1}$) of a polyprotic acid. The reason for this is that it is more difficult to remove a positively charged proton from a negative ion due to electrostatic forces. This can be seen in the case of removing a proton from the uncharged $H_2CO_3$ as compared from a negatively charged $HCO_3^-$. Similarly, it is more difficult to remove a proton from a doubly charged $HPO_4^{2-}$ anion as compared to $H_2PO_4^-$. Polyprotic acid solutions contain a mixture of acids like $H_2A$, $HA^-$ and $A^{2-}$ in case of a diprotic acid. $H_2A$ being a strong acid, the primary reaction involves the dissociation of $H_2A$, and $H_3O^+$ in the solution comes mainly from the first dissociation step. 6.11.7 Factors Affecting Acid Strength Having discussed quantitatively the strengths of acids and bases, we come to a stage where we can calculate the pH of a given acid solution. But, the curiosity rises about why should some acids be stronger than others? What factors are responsible for making them stronger? The answer lies in its being a complex phenomenon. But, broadly speaking we can say that the extent of dissociation of an acid depends on the strength and polarity of the H-A bond. Rationalised 2023-24 EQUILIBRIUM 201 of common ion effect. It can be defined as a shift in equilibrium on adding a substance that provides more of an ionic species already present in the dissociation equilibrium. Thus, we can say that common ion effect is a phenomenon based on the Le Chatelier's principle discussed in section

6.8. In order to evaluate the pH of the solution resulting on addition of 0.05M acetate ion to 0.05M acetic acid solution, we shall consider the acetic acid dissociation equilibrium once again, HAc(aq) H+(aq) + Ac– (aq) Initial concentration (M) 0.05 0 0.05 Let x be the extent of ionization of acetic acid. Change in concentration (M) –x +x +x Equilibrium concentration (M) 0.05-x x 0.05+x Therefore, Ka= [H+][Ac– ]/[H Ac] = {(0.05+x)(x)}/(0.05-x) As Ka is small for a very weak acid, x< 0.1M Category II Slightly 0.01M<Solubility< 0.1M Soluble Category III Sparingly Solubility < 0.01M Soluble We shall now consider the equilibrium between the sparingly soluble ionic salt and its saturated aqueous solution. 6.13.1 Solubility Product Constant Let us now have a solid like barium sulphate in contact with its saturated aqueous solution. The equilibrium between the undisolved solid and the ions in a saturated solution can be represented by the equation: BaSO4(s) Ba2+(aq) + SO4 2–(aq), The equilibrium constant is given by the equation: K = {[Ba2+][SO4 2–]} / [BaSO4] For a pure solid substance the concentration remains constant and we can write Ksp = K[BaSO4] = [Ba2+][SO4 2–] (6.43) We call Ksp the solubility product constant or simply solubility product. The experimental value of Ksp in above equation at 298K is 1.1×10–10. This means that for solid barium sulphate in equilibrium with its saturated solution, the product of the concentrations of barium and sulphate ions is equal to its solubility product constant. The concentrations of the two ions will be equal to the molar solubility of the barium sulphate. If molar solubility is S, then $1.1 \times 10^{-10} = (S)(S) = S^2$ or S = $1.05 \times 10^{-5}$. Thus, molar solubility of barium sulphate will be equal to $1.05 \times 10^{-5}$ mol L–1. A salt may give on dissociation two or more than two anions and cations carrying different charges. For example, consider a salt like zirconium phosphate of molecular formula (Zr4+) 3(PO4 3–) 4. It dissociates into 3 zirconium cations of charge +4 and 4 phosphate anions of charge –3. If the molar solubility of zirconium phosphate is S, then it can be seen from the stoichiometry of the compound that [Zr4+] = 3S and [PO4 3–] = 4S and Ksp = (3S)3 (4S)4 = 6912 (S)7 or S = {Ksp / (33 × 44)}1/7 = (Ksp / 6912)1/7 Rationalised 2023-24 EQUILIBRIUM 205 A solid salt of the general formula M X x p y  - q with molar solubility S in equilibrium with its saturated solution may be represented by the equation: Mx Xy (s) xMp+(aq) + yXq– (aq) (where x × p+ = y × q– ) And its solubility product constant is given by: Ksp = [Mp+] x [Xq– ] y = (xS)x (yS)y (6.44) = xx . yy . S(x + y) S(x + y) = Ksp / xx . yy S = (Ksp / xx . yy ) 1 / x + y (6.45) The term Ksp in equation is given by Qsp (section 6.6.2) when the concentration of one or more species is not the concentration under equilibrium. Obviously under equilibrium conditions Ksp = Qsp but otherwise it gives the direction of the processes of precipitation or dissolution. The solubility product constants of a number of common salts at 298K are given in Table 6.9. Table 6.9 The Solubility Product Constants, Ksp of Some Common Ionic Salts at 298K. Problem 6.26 Calculate the solubility of A2X3 in pure water, assuming that neither kind of ion reacts with water. The solubility product of A2X3, Ksp = 1.1 × 10–23. Solution A2X3 → 2A3+ + 3X2– Ksp = [A3+] 2 [X2–] 3 = 1.1 × 10–23 If S = solubility of A2X3, then [A3+] = 2S; [X2–] = 3S therefore, Ksp = (2S)2(3S)3 = 108S5 = 1.1 × 10–23 thus, S5 = 1 × 10–25 S = 1.0 × 10–5 mol/L. Problem 6.27 The values of Ksp of two sparingly soluble salts Ni(OH)2 and AgCN are 2.0 × 10–15 and 6 × 0–17 respectively. Which salt is more soluble? Explain. Solution AgCN Ag+ + CN– Rationalised 2023-24 206 chemistry Ksp = [Ag+][CN– ] = 6 × 10–17 Ni(OH)2 Ni2+ + 2OH– Ksp = [Ni2+][OH– ] 2 = 2 × 10–15 Let [Ag+] = S1, then [CN- ] = S1 Let [Ni2+] = S2, then [OH– ] = 2S2 S1 2 = 6 × 10–17 , S1 = 7.8 × 10–9 (S2)(2S2) 2 = 2 × 10–15, S2 = 0.58 × 10–4 Ni(OH)2 is more soluble than AgCN. 6.13.2 Common Ion Effect on Solubility of Ionic Salts It is expected from Le Chatelier's principle that if we increase the concentration of any one of the ions, it should combine with the ion of its opposite charge and some of the salt will be precipitated till once again Ksp = Qsp. Similarly, if the concentration of one of the ions is decreased, more salt will dissolve to increase the concentration of both the ions till once again Ksp = Qsp. This is applicable even to soluble salts like sodium chloride except that due to higher concentrations of the ions, we use their activities instead of their molarities in the expression for Qsp. Thus if we take a saturated solution of sodium chloride and pass HCl gas through it, then sodium chloride is

precipitated due to increased concentration (activity) of chloride ion available from the dissociation of HCl. Sodium chloride thus obtained is of very high purity and we can get rid of impurities like sodium and magnesium sulphates. The common ion effect is also used for almost complete precipitation of a particular ion as its sparingly soluble salt, with very low value of solubility product for gravimetric estimation. Thus we can precipitate silver ion as silver chloride, ferric ion as its hydroxide (or hydrated ferric oxide) and barium ion as its sulphate for quantitative estimations. Dissolution of S mol/L of Ni(OH)2 provides S mol/L of Ni2+ and 2S mol/L of OH− , but the total concentration of OH− = (0.10 + 2S) mol/L because the solution already contains 0.10 mol/L of OH− from NaOH. Ksp = 2.0 × 10–15 = [Ni2+] [OH− ] 2 = (S) (0.10 + 2S)2 As Ksp is small, 2S << 0.10, thus, (0.10 + 2S) ≈ 0.10 Hence, 2.0 × 10–15 = S (0.10)2 S = 2.0 × 10–13 M = [Ni2+] Problem 6.28 Calculate the molar solubility of Ni(OH)2 in 0.10 M NaOH. The ionic product of Ni(OH)2 is 2.0 × 10–15. Solution Let the solubility of Ni(OH)2 be equal to S. The solubility of salts of weak acids like phosphates increases at lower pH. This is because at lower pH the concentration of the anion decreases due to its protonation. This in turn increase the solubility of the salt so that Ksp = Qsp. We have to satisfy two equilibria simultaneously i.e., Ksp = [M+] [X− ], [X− ] / [HX] = Ka/[H+] Taking inverse of both side and adding 1 we get HX X H HX H X H a a a - 🔲🔲🔲🔲🔲🔲🔲🔲🔲🔲🔲 - 🔲🔲🔲🔲🔲🔲🔲🔲🔲🔲🔲🔲🔲🔲🔲🔲🔲🔲 🔲 1 1 K K K Now, again taking inverse, we get [X− ] / {[X− ] + [HX]} = f = Ka/(Ka + [H+]) and it can be seen that 'f' decreases as pH decreases. If S is the solubility of the salt at a given pH then Ksp = [S] [f S] = S2 {Ka/(Ka + [H+])} and S = {Ksp ([H+] + Ka)/Ka} 1/2 (6.46) Thus solubility S increases with increase in [H+] or decrease in pH. Rationalised 2023-24 EQUILIBRIUM 207 SUMMARY When the number of molecules leaving the liquid to vapour equals the number of molecules returning to the liquid from vapour, equilibrium is said to be attained and is dynamic in nature. Equilibrium can be established for both physical and chemical processes and at this stage rate of forward and reverse reactions are equal. Equilibrium constant, Kc is expressed as the concentration of products divided by reactants, each term raised to the stoichiometric coefficient. For reaction, a A + b B c C +d D Kc = [C]c [D]d/[A]a[B]b Equilibrium constant has constant value at a fixed temperature and at this stage all the macroscopic properties such as concentration, pressure, etc. become constant. For a gaseous reaction equilibrium constant is expressed as Kp and is written by replacing concentration terms by partial pressures in Kc expression. The direction of reaction can be predicted by reaction quotient Qc which is equal to Kc at equilibrium. Le Chatelier's principle states that the change in any factor such as temperature, pressure, concentration, etc. will cause the equilibrium to shift in such a direction so as to reduce or counteract the effect of the change. It can be used to study the effect of various factors such as temperature, concentration, pressure, catalyst and inert gases on the direction of equilibrium and to control the yield of products by controlling these factors. Catalyst does not effect the equilibrium composition of a reaction mixture but increases the rate of chemical reaction by making available a new lower energy pathway for conversion of reactants to products and vice-versa. All substances that conduct electricity in aqueous solutions are called electrolytes. Acids, bases and salts are electrolytes and the conduction of electricity by their aqueous solutions is due to anions and cations produced by the dissociation or ionization of electrolytes in aqueous solution. The strong electrolytes are completely dissociated. In weak electrolytes there is equilibrium between the ions and the unionized electrolyte molecules. According to Arrhenius, acids give hydrogen ions while bases produce hydroxyl ions in their aqueous solutions. Brönsted-Lowry on the other hand, defined an acid as a proton donor and a base as a proton acceptor. When a Brönsted-Lowry acid reacts with a base, it produces its conjugate base and a conjugate acid corresponding to the base with which it reacts. Thus a conjugate pair of acid-base differs only by one proton. Lewis further generalised the definition of an acid as an electron pair acceptor and a base as an electron pair donor. The expressions for ionization (equilibrium) constants of weak acids (Ka) and weak bases (Kb) are developed using Arrhenius definition. The degree of ionization and its dependence on concentration

and common ion are discussed. The pH scale (pH = –log[H+]) for the hydrogen ion concentration (activity) has been introduced and extended to other quantities (pOH = – log[OH– ]); pKa = –log[Ka ]; pKb = –log[Kb]; and pKw = –log[Kw] etc.). The ionization of water has been considered and we note that the equation: pH + pOH = pKw is always satisfied. The salts of strong acid and weak base, weak acid and strong base, and weak acid and weak base undergo hydrolysis in aqueous solution. The definition of buffer solutions, and their importance are discussed briefly. The solubility equilibrium of sparingly soluble salts is discussed and the equilibrium constant is introduced as solubility product constant (Ksp). Its relationship with solubility of the salt is established. The conditions of precipitation of the salt from their solutions or their dissolution in water are worked out. The role of common ion and the solubility of sparingly soluble salts is also discussed. Rationalised 2023-24 208 chemistry SUGGESTED ACTIVITIES FOR STUDENTS REGARDING THIS UNIT (a) The student may use pH paper in determining the pH of fresh juices of various vegetables and fruits, soft drinks, body fluids and also that of water samples available. (b) The pH paper may also be used to determine the pH of different salt solutions and from that he/she may determine if these are formed from strong/weak acids and bases. (c) They may prepare some buffer solutions by mixing the solutions of sodium acetate and acetic acid and determine their pH using pH paper. (d) They may be provided with different indicators to observe their colours in solutions of varying pH. (e) They may perform some acid-base titrations using indicators. (f) They may observe common ion effect on the solubility of sparingly soluble salts. (g) If pH meter is available in their school, they may measure the pH with it and compare the results obtained with that of the pH paper. EXERCISES 6.1 A liquid is in equilibrium with its vapour in a sealed container at a fixed temperature. The volume of the container is suddenly increased. a) What is the initial effect of the change on vapour pressure? b) How do rates of evaporation and condensation change initially? c) What happens when equilibrium is restored finally and what will be the final vapour pressure? 6.2 What is Kc for the following equilibrium when the equilibrium concentration of each substance is: [SO2]= 0.60M, [O2] = 0.82M and [SO3] = 1.90M ? $2SO_2(g) + O_2(g)$ $2SO_3(g)$ 6.3 At a certain temperature and total pressure of $10^5$Pa, iodine vapour contains 40% by volume of I atoms $I_2$ (g) $2I$ (g) Calculate Kp for the equilibrium. 6.4 Write the expression for the equilibrium constant, Kc for each of the following reactions: (i) $2NOCl$ (g) $2NO$ (g) + $Cl_2$ (g) (ii) $2Cu(NO_3)_2$ (s) $2CuO$ (s) + $4NO_2$ (g) + $O_2$ (g) (iii) $CH_3COOC_2H_5(aq) + H_2O(l)$ $CH_3COOH$ (aq) + $C_2H_5OH$ (aq) (iv) $Fe^{3+}$ (aq) + $3OH^–$ (aq) $Fe(OH)_3$ (s) (v) $I_2$ (s) + $5F_2$ $2IF_5$ 6.5 Find out the value of Kc for each of the following equilibria from the value of Kp: (i) $2NOCl$ (g) $2NO$ (g) + $Cl_2$ (g); Kp= $1.8 \times 10^{–2}$ at 500 K (ii) $CaCO_3$ (s) $CaO(s) + CO_2(g)$; Kp= 167 at 1073 K Rationalised 2023-24 EQUILIBRIUM 209 6.6 For the following equilibrium, Kc = $6.3 \times 10^{14}$ at 1000 K $NO$ (g) + $O_3$ (g) $NO_2$ (g) + $O_2$ (g) Both the forward and reverse reactions in the equilibrium are elementary bimolecular reactions. What is Kc , for the reverse reaction? 6.7 Explain why pure liquids and solids can be ignored while writing the equilibrium constant expression? 6.8 Reaction between N2 and O2– takes place as follows: $2N_2$ (g) + $O_2$ (g) $2N_2O$ (g) If a mixture of 0.482 mol N2 and 0.933 mol of O2 is placed in a 10 L reaction vessel and allowed to form N2O at a temperature for which Kc = $2.0 \times 10^{–37}$, determine the composition of equilibrium mixture. 6.9 Nitric oxide reacts with Br2 and gives nitrosyl bromide as per reaction given below: $2NO$ (g) + $Br_2$ (g) $2NOBr$ (g) When 0.087 mol of NO and 0.0437 mol of Br2 are mixed in a closed container at constant temperature, 0.0518 mol of NOBr is obtained at equilibrium. Calculate equilibrium amount of NO and Br2 . 6.10 At 450K, Kp= $2.0 \times 10^{10}$/bar for the given reaction at equilibrium. $2SO_2(g) + O_2(g)$ $2SO_3$ (g) What is Kc at this temperature ? 6.11 A sample of HI(g) is placed in flask at a pressure of 0.2 atm. At equilibrium the partial pressure of HI(g) is 0.04 atm. What is Kp for the given equilibrium ? $2HI$ (g) $H_2$ (g) + $I_2$ (g) 6.12 A mixture of 1.57 mol of N2, 1.92 mol of H2 and 8.13 mol of NH3 is introduced into a 20 L reaction vessel at 500 K. At this temperature, the equilibrium constant, Kc for the reaction $N_2$ (g) + $3H_2$ (g) $2NH_3$ (g) is $1.7 \times 10^2$. Is the reaction mixture at equilibrium? If not, what is the direction of the net reaction? 6.13 The equilibrium

constant expression for a gas reaction is, Kc $= \dfrac{[NH_3]^4[O_2]^5}{[NO]^4[H_2O]^6}$ Write the balanced chemical equation corresponding to this expression.

6.14 One mole of $H_2O$ and one mole of CO are taken in 10 L vessel and heated to 725 K. At equilibrium 40% of water (by mass) reacts with CO according to the equation, $H_2O$ (g) + CO (g) ⇌ $H_2$ (g) + $CO_2$ (g) Calculate the equilibrium constant for the reaction.

6.15 At 700 K, equilibrium constant for the reaction: $H_2$ (g) + $I_2$ (g) ⇌ 2HI (g) is 54.8. If 0.5 mol L⁻¹ of HI(g) is present at equilibrium at 700 K, what are the concentration of $H_2$(g) and $I_2$(g) assuming that we initially started with HI(g) and allowed it to reach equilibrium at 700K?

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6.16 What is the equilibrium concentration of each of the substances in the equilibrium when the initial concentration of ICl was 0.78 M ? 2ICl (g) ⇌ $I_2$ (g) + $Cl_2$ (g); Kc = 0.14

6.17 Kp = 0.04 atm at 899 K for the equilibrium shown below. What is the equilibrium concentration of $C_2H_6$ when it is placed in a flask at 4.0 atm pressure and allowed to come to equilibrium? $C_2H_6$ (g) ⇌ $C_2H_4$ (g) + $H_2$ (g)

6.18 Ethyl acetate is formed by the reaction between ethanol and acetic acid and the equilibrium is represented as: $CH_3COOH$ (l) + $C_2H_5OH$ (l) ⇌ $CH_3COOC_2H_5$ (l) + $H_2O$ (l)
(i) Write the concentration ratio (reaction quotient), Qc , for this reaction (note: water is not in excess and is not a solvent in this reaction)
(ii) At 293 K, if one starts with 1.00 mol of acetic acid and 0.18 mol of ethanol, there is 0.171 mol of ethyl acetate in the final equilibrium mixture. Calculate the equilibrium constant.
(iii) Starting with 0.5 mol of ethanol and 1.0 mol of acetic acid and maintaining it at 293 K, 0.214 mol of ethyl acetate is found after sometime. Has equilibrium been reached?

6.19 A sample of pure $PCl_5$ was introduced into an evacuated vessel at 473 K. After equilibrium was attained, concentration of $PCl_5$ was found to be 0.5 × 10⁻¹ mol L⁻¹. If value of Kc is 8.3 × 10⁻³, what are the concentrations of $PCl_3$ and $Cl_2$ at equilibrium? $PCl_5$ (g) ⇌ $PCl_3$ (g) + $Cl_2$(g)

6.20 One of the reaction that takes place in producing steel from iron ore is the reduction of iron(II) oxide by carbon monoxide to give iron metal and $CO_2$. FeO (s) + CO (g) ⇌ Fe (s) + $CO_2$ (g); Kp = 0.265 atm at 1050K What are the equilibrium partial pressures of CO and $CO_2$ at 1050 K if the initial partial pressures are: pCO= 1.4 atm and $p_{CO_2}$ = 0.80 atm?

6.21 Equilibrium constant, Kc for the reaction $N_2$ (g) + $3H_2$ (g) ⇌ $2NH_3$ (g) at 500 K is 0.061 At a particular time, the analysis shows that composition of the reaction mixture is 3.0 mol L⁻¹ $N_2$, 2.0 mol L⁻¹ $H_2$ and 0.5 mol L⁻¹ $NH_3$. Is the reaction at equilibrium? If not in which direction does the reaction tend to proceed to reach equilibrium?

6.22 Bromine monochloride, BrCl decomposes into bromine and chlorine and reaches the equilibrium: 2BrCl (g) ⇌ $Br_2$ (g) + $Cl_2$ (g) for which Kc = 32 at 500 K. If initially pure BrCl is present at a concentration of 3.3 × 10⁻³ mol L⁻¹, what is its molar concentration in the mixture at equilibrium?

6.23 At 1127 K and 1 atm pressure, a gaseous mixture of CO and $CO_2$ in equilibrium with soild carbon has 90.55% CO by mass C (s) + $CO_2$ (g) ⇌ 2CO (g) Calculate Kc for this reaction at the above temperature.

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6.24 Calculate a) ΔG0 and b) the equilibrium constant for the formation of $NO_2$ from NO and $O_2$ at 298K NO (g) + ½ $O_2$ (g) ⇌ $NO_2$ (g) where Δf G0 ($NO_2$) = 52.0 kJ/mol Δf G0 (NO) = 87.0 kJ/mol Δf G0 ($O_2$) = 0 kJ/mol

6.25 Does the number of moles of reaction products increase, decrease or remain same when each of the following equilibria is subjected to a decrease in pressure by increasing the volume? (a) $PCl_5$ (g) ⇌ $PCl_3$ (g) + $Cl_2$ (g) (b) CaO (s) + $CO_2$ (g) ⇌ $CaCO_3$ (s) (c) 3Fe (s) + $4H_2O$ (g) ⇌ $Fe_3O_4$ (s) + $4H_2$ (g)

6.26 Which of the following reactions will get affected by increasing the pressure? Also, mention whether change will cause the reaction to go into forward or backward direction. (i) $COCl_2$ (g) ⇌ CO (g) + $Cl_2$ (g) (ii) $CH_4$ (g) + $2S_2$ (g) ⇌ $CS_2$ (g) + $2H_2S$ (g) (iii) $CO_2$ (g) + C (s) ⇌ 2CO (g) (iv) $2H_2$ (g) + CO (g) ⇌ $CH_3OH$ (g) (v) $CaCO_3$ (s) ⇌ CaO (s) + $CO_2$ (g) (vi) 4 $NH_3$ (g) + $5O_2$ (g) ⇌ 4NO (g) + $6H_2O$(g)

6.27 The equilibrium constant for the following reaction is 1.6 ×10⁵ at 1024K $H_2$(g) + $Br_2$(g) ⇌ 2HBr(g) Find the equilibrium pressure of all gases if 10.0 bar of HBr is introduced into a sealed container at 1024K.

6.28 Dihydrogen gas is obtained from natural gas by partial oxidation with steam as per following endothermic reaction: $CH_4$ (g) + $H_2O$ (g) ⇌ CO (g) + $3H_2$ (g) (a) Write as expression for Kp for the above reaction. (b) How will the values of Kp and composition of equilibrium mixture be affected by (i) increasing the pressure (ii) increasing the temperature (iii) using a catalyst?

6.29

Describe the effect of: a) addition of $H_2$ b) addition of $CH_3OH$ c) removal of CO d) removal of $CH_3OH$ on the equilibrium of the reaction: $2H_2(g)$ + CO (g) $CH_3OH$ (g) 6.30 At 473 K, equilibrium constant $K_c$ for decomposition of phosphorus pentachloride, $PCl_5$ is $8.3 \times 10^{-3}$. If decomposition is depicted as, Rationalised 2023-24 212 chemistry $PCl_5$ (g) $PCl_3$ (g) + $Cl_2$ (g) $\Delta_r H^0$ = 124.0 kJ mol$^{-1}$ a) write an expression for $K_c$ for the reaction. b) what is the value of $K_c$ for the reverse reaction at the same temperature? c) what would be the effect on $K_c$ if (i) more $PCl_5$ is added (ii) pressure is increased (iii) the temperature is increased ? 6.31 Dihydrogen gas used in Haber's process is produced by reacting methane from natural gas with high temperature steam. The first stage of two stage reaction involves the formation of CO and $H_2$. In second stage, CO formed in first stage is reacted with more steam in water gas shift reaction, CO (g) + $H_2O$ (g) $CO_2$ (g) + $H_2$ (g) If a reaction vessel at 400°C is charged with an equimolar mixture of CO and steam such that $p_{co}$ = $p_{H_2O}$ = 4.0 bar, what will be the partial pressure of $H_2$ at equilibrium? $K_p$= 10.1 at 400°C 6.32 Predict which of the following reaction will have appreciable concentration of reactants and products: a) $Cl_2$ (g) 2Cl (g) $K_c$ = $5 \times 10^{-39}$ b) $Cl_2$ (g) + 2NO (g) 2NOCl (g) $K_c$ = $3.7 \times 10^8$ c) $Cl_2$ (g) + $2NO_2$ (g) $2NO_2Cl$ (g) $K_c$ = 1.8 6.33 The value of $K_c$ for the reaction $3O_2$ (g) $2O_3$ (g) is $2.0 \times 10^{-50}$ at 25°C. If the equilibrium concentration of $O_2$ in air at 25°C is $1.6 \times 10^{-2}$, what is the concentration of $O_3$? 6.34 The reaction, CO(g) + $3H_2$(g) $CH_4$(g) + $H_2O$(g) is at equilibrium at 1300 K in a 1L flask. It also contain 0.30 mol of CO, 0.10 mol of $H_2$ and 0.02 mol of $H_2O$ and an unknown amount of $CH_4$ in the flask. Determine the concentration of $CH_4$ in the mixture. The equilibrium constant, $K_c$ for the reaction at the given temperature is 3.90. 6.35 What is meant by the conjugate acid-base pair? Find the conjugate acid/base for the following species: $HNO_2$, CN$^-$ , $HClO_4$, F $^-$ , OH$^-$ , CO , and S$^{2-}$ 6.36 Which of the followings are Lewis acids? $H_2O$, $BF_3$, H+, and $NH_4$ + 6.37 What will be the conjugate bases for the Brönsted acids: HF, $H_2SO_4$ and HCO$^-$ 3? 6.38 Write the conjugate acids for the following Brönsted bases: $NH_2$ $^-$ , $NH_3$ and HCOO$^-$ . 6.39 The species: $H_2O$, $HCO_3$ $^-$ , $HSO_4$ $^-$ and $NH_3$ can act both as Brönsted acids and bases. For each case give the corresponding conjugate acid and base. 6.40 Classify the following species into Lewis acids and Lewis bases and show how these act as Lewis acid/base: (a) OH$^-$ (b) F$^-$ (c) H+ (d) $BCl_3$ . 6.41 The concentration of hydrogen ion in a sample of soft drink is $3.8 \times 10^{-3}$ M. What is its pH? 6.42 The pH of a sample of vinegar is 3.76. Calculate the concentration of hydrogen ion in it. 6.43 The ionization constant of HF, HCOOH and HCN at 298K are $6.8 \times 10^{-4}$, $1.8 \times 10^{-4}$ and $4.8 \times 10^{-9}$ respectively. Calculate the ionization constants of the corresponding conjugate base. Rationalised 2023-24 EQUILIBRIUM 213 6.44 The ionization constant of phenol is $1.0 \times 10^{-10}$. What is the concentration of phenolate ion in 0.05 M solution of phenol? What will be its degree of ionization if the solution is also 0.01M in sodium phenolate? 6.45 The first ionization constant of $H_2S$ is $9.1 \times 10^{-8}$. Calculate the concentration of HS$^-$ ion in its 0.1M solution. How will this concentration be affected if the solution is 0.1M in HCl also? If the second dissociation constant of $H_2S$ is $1.2 \times 10^{-13}$, calculate the concentration of S$^{2-}$ under both conditions. 6.46 The ionization constant of acetic acid is $1.74 \times 10^{-5}$. Calculate the degree of dissociation of acetic acid in its 0.05 M solution. Calculate the concentration of acetate ion in the solution and its pH. 6.47 It has been found that the pH of a 0.01M solution of an organic acid is 4.15. Calculate the concentration of the anion, the ionization constant of the acid and its pKa. 6.48 Assuming complete dissociation, calculate the pH of the following solutions: (a) 0.003 M HCl (b) 0.005 M NaOH (c) 0.002 M HBr (d) 0.002 M KOH 6.49 Calculate the pH of the following solutions: a) 2 g of TlOH dissolved in water to give 2 litre of solution. b) 0.3 g of $Ca(OH)_2$ dissolved in water to give 500 mL of solution. c) 0.3 g of NaOH dissolved in water to give 200 mL of solution. d) 1mL of 13.6 M HCl is diluted with water to give 1 litre of solution. 6.50 The degree of ionization of a 0.1M bromoacetic acid solution is 0.132. Calculate the pH of the solution and the pKa of bromoacetic acid. 6.51 The pH of 0.005M codeine ($C_{18}H_{21}NO_3$) solution is 9.95. Calculate its ionization constant and pKb. 6.52 What is the pH of 0.001M aniline solution? The ionization constant of aniline can be taken from Table 6.7. Calculate the degree of ionization of aniline in the solution.

Also calculate the ionization constant of the conjugate acid of aniline. 6.53 Calculate the degree of ionization of 0.05M acetic acid if its pKa value is 4.74. How is the degree of dissociation affected when its solution also contains (a) 0.01M (b) 0.1M in HCl ? 6.54 The ionization constant of dimethylamine is $5.4 \times 10^{-4}$. Calculate its degree of ionization in its 0.02M solution. What percentage of dimethylamine is ionized if the solution is also 0.1M in NaOH? 6.55 Calculate the hydrogen ion concentration in the following biological fluids whose pH are given below: (a) Human muscle-fluid, 6.83 (b) Human stomach fluid, 1.2 (c) Human blood, 7.38 (d) Human saliva, 6.4. 6.56 The pH of milk, black coffee, tomato juice, lemon juice and egg white are 6.8, 5.0, 4.2, 2.2 and 7.8 respectively. Calculate corresponding hydrogen ion concentration in each. 6.57 If 0.561 g of KOH is dissolved in water to give 200 mL of solution at 298 K. Calculate the concentrations of potassium, hydrogen and hydroxyl ions. What is its pH? 6.58 The solubility of $Sr(OH)_2$ at 298 K is 19.23 g/L of solution. Calculate the concentrations of strontium and hydroxyl ions and the pH of the solution. Rationalised 2023-24 214 chemistry 6.59 The ionization constant of propanoic acid is $1.32 \times 10^{-5}$. Calculate the degree of ionization of the acid in its 0.05M solution and also its pH. What will be its degree of ionization if the solution is 0.01M in HCl also? 6.60 The pH of 0.1M solution of cyanic acid (HCNO) is 2.34. Calculate the ionization constant of the acid and its degree of ionization in the solution. 6.61 The ionization constant of nitrous acid is $4.5 \times 10^{-4}$. Calculate the pH of 0.04 M sodium nitrite solution and also its degree of hydrolysis. 6.62 A 0.02M solution of pyridinium hydrochloride has pH = 3.44. Calculate the ionization constant of pyridine. 6.63 Predict if the solutions of the following salts are neutral, acidic or basic: NaCl, KBr, NaCN, NH4NO3, NaNO2 and KF 6.64 The ionization constant of chloroacetic acid is $1.35 \times 10^{-3}$. What will be the pH of 0.1M acid and its 0.1M sodium salt solution? 6.65 Ionic product of water at 310 K is $2.7 \times 10^{-14}$. What is the pH of neutral water at this temperature? 6.66 Calculate the pH of the resultant mixtures: a) 10 mL of 0.2M Ca(OH)2 + 25 mL of 0.1M HCl b) 10 mL of 0.01M H2SO4 + 10 mL of 0.01M Ca(OH)2 c) 10 mL of 0.1M H2SO4 + 10 mL of 0.1M KOH 6.67 Determine the solubilities of silver chromate, barium chromate, ferric hydroxide, lead chloride and mercurous iodide at 298K from their solubility product constants given in Table 6.9. Determine also the molarities of individual ions. 6.68 The solubility product constant of Ag2CrO4 and AgBr are $1.1 \times 10^{-12}$ and $5.0 \times 10^{-13}$ respectively. Calculate the ratio of the molarities of their saturated solutions. 6.69 Equal volumes of 0.002 M solutions of sodium iodate and cupric chlorate are mixed together. Will it lead to precipitation of copper iodate? (For cupric iodate Ksp = $7.4 \times 10^{-8}$ ). 6.70 The ionization constant of benzoic acid is $6.46 \times 10^{-5}$ and Ksp for silver benzoate is $2.5 \times 10^{-13}$. How many times is silver benzoate more soluble in a buffer of pH 3.19 compared to its solubility in pure water? 6.71 What is the maximum concentration of equimolar solutions of ferrous sulphate and sodium sulphide so that when mixed in equal volumes, there is no precipitation of iron sulphide? (For iron sulphide, Ksp = $6.3 \times 10^{-18}$). 6.72 What is the minimum volume of water required to dissolve 1g of calcium sulphate at 298 K? (For calcium sulphate, Ksp is $9.1 \times 10^{-6}$). 6.73 The concentration of sulphide ion in 0.1M HCl solution saturated with hydrogen sulphide is $1.0 \times 10^{-19}$ M. If 10 mL of this is added to 5 mL of 0.04 M solution of the following: FeSO4, MnCl2, ZnCl2 and CdCl2. in which of these solutions precipitation will take place? Rationalised 2023-24Unit 7 7.25 15 g Unit 8 8.32 Mass of carbon dioxide formed = 0.505 g Mass of water formed = 0.0864 g 8.33 % fo nitrogen = 56 8.34 % of chlorine = 37.57 8.35 % of sulphur = 19.66 Unit 9 9.1 Due to the side reaction in termination step by the combination of two C. H3 free radicals. 9.2 (a) 2-Methyl-but-2-ene (b) Pent-1-ene-3-yne (c) Buta-1, 3-diene (d) 4-Phenylbut-1-ene (e) 2-Methylphenol (f) 5-(2-Methylpropyl)-decane (g) 4-Ethyldeca –1,5,8- triene 9.3 (a) (i) $CH_2 = CH - CH_2 - CH_3$ But-1-ene (ii) $CH_3 - CH_2 = CH - CH_3$ But-2-ene (iii) $CH_2 = C - CH_3$ 2-Methylpropene | CH3 (b) (i) $HC \equiv C - CH_2 - CH_2 - CH_3$ Pent-1-yne (ii) $CH_3 - C \equiv C - CH_2 - CH_3$ Pent-2-yne (iii) $CH_3 - CH - C \equiv CH$ 3-Methylbut-1-yne | CH3 9.4 (i) Ethanal and propanal (ii) Butan-2-one and pentan-2-one (iii) Methanal and pentan-3-one (iv) Propanal and benzaldehyde 9.5 3-Ethylpent-2-ene 9.6 But-2-ene 9.7

4-Ethylhex-3-ene CH3 – CH2– C = CH – CH2–CH3 | CH2–CH3 Answer to Some Selected Problems

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9.8 (a) C4H10(g)+13/2O2(g) $\Delta$ 4CO2(g) + 5H2O(g) (b) C5H10(g)+15/2O2(g) $\Delta$ 5CO2(g) + 5H2O(g) (c) C5H10(g) + 17/2 O2(g) $\Delta$ 6CO2(g) + 5H2O(g) (d) C7H8(g) + 9O2(g) $\Delta$ 7CO2(g) + 4H2O(g) cis-Hex-2-ene trans-Hex-2-ene The cis form will have higher boiling point due to more polar nature leading to stronger intermolecular dipole–dipole interaction, thus requiring more heat energy to separate them. 9.10 Due to resonance 9.11 Planar, conjugated ring system with delocalisation of (4n+2) electrons, where, n is an integer 9.12 Lack of delocalisation of (4n +2) $\pi$ electrons in the cyclic system. 9.13 (i) (ii) Rationalised 2023-24 330 chemistry (iii) (iv) 9.14 15 H attached to 1° carbons 4 H attached to 2° carbons 1 H attached to 3° carbons 9.15 More the branching in alkane, lower will be the boiling point. 9.16 Refer to addition reaction of HBr to unsymmetrical alkenes in the text. All the three products cannot be obtained by any one of the Kekulé's structures. This shows that benzene is a resonance hybrid of the two resonating structures. 9.18 H – C $\equiv$ C – H > C6H6 > C6H14. Due to maximum s orbital character in enthyne (50 per cent) as compared to 33 per cent in benzene and 25 per cent in n-hexane. 9.19 Due to the presence of 6 $\pi$ electrons, benzene behaves as a rich source of electrons thus being easily attacked by reagents deficient in electrons. Rationalised 2023-24 answers 331 9.20 (i) (ii) C2H4 Br2 CH2–CH2 alc, KOH CH2=CHNr NaNH2 Br BR (iii) CH3 | 9.21 CH2 = C – CH2 – CH3 2-Methylbut-1-ene CH3 | CH3 – C = CH – CH3 2-Methylbut-2-ene CH3 | CH3 – CH –CH = CH2 3-Methylbut-1-ene 9.22 (a) Chlorobenzene>p-nitrochlorobenzene> 2,4 – dinitrochlorobenzene (b) Toluene > p-CH3-C6H4-NO2 > p-O2N–C6H4–NO2 9.23 Toleune undergoes nitration most easily due to electron releasing nature of the methyl group. 9.24 FeCl3 9.25 Due to the formation of side products. For example, by starting with 1-bromopropane and 1-bromobutane, hexane and octane are the side products besides heptane. Rationalised 2023-24

answerS 3 Foreword The National Curriculum Framework (NCF), 2005 recommends that children's life at school must be

linked to their life outside the school. This principle marks a departure from the legacy of bookish learning which continues to shape our system and causes a gap between the school, home and community. The syllabi and textbooks developed on the basis of NCF signify an attempt to implement this basic idea. They also attempt to discourage rote learning and the maintenance of sharp boundaries between different subject areas. We hope these measures will take us significantly further in the direction of a child-centred system of education outlined in the National Policy on Education (1986). The success of this effort depends on the steps that school principals and teachers will take to encourage children to reflect on their own learning and to pursue imaginative activities and questions. We must recognise that, given space, time and freedom, children generate new knowledge by engaging with the information passed on to them by adults. Treating the prescribed textbook as the sole basis of examination is one of the key reasons why other resources and sites of learning are ignored. Inculcating creativity and initiative is possible if we perceive and treat children as participants in learning, not as receivers of a fixed body of knowledge. These aims imply considerable change in school routines and mode of functioning. Flexibility in the daily time-table is as necessary as rigour in implementing the annual calender so that the required number of teaching days are actually devoted to teaching. The methods used for teaching and evaluation will also determine how effective this textbook proves for making children's life at school a happy experience, rather than a source of stress or boredom. Syllabus designers have tried to address the problem of curricular burden by restructuring and reorienting knowledge at different stages with greater consideration for child psychology and the time available for teaching. The textbook attempts to enhance this endeavour by giving higher priority and space to opportunities for contemplation and wondering, discussion in small groups, and activities requiring hands-on experience. The National Council of Educational Research and Training (NCERT) appreciates the hard work done by the textbook development committee responsible for this book. We wish to thank the Chairperson of the advisory group in science and mathematics, Professor J.V. Narlikar and the Chief Advisor for this book, Professor B. L. Khandelwal for guiding the work of this committee. Several teachers contributed to the development of this textbook; we are grateful to their principals for making this possible. We are indebted to the institutions and organisations which have generously permitted us to draw upon their resources, material and personnel. We are especially grateful to the members of the National Monitoring Committee, appointed by the Department of Secondary and Higher Education, Ministry of Human Resource Development under the Chairpersonship of Professor Mrinal Miri and Professor G.P. Deshpande, for their valuable time and contribution. As an organisation committed to systemic reform and continuous improvement in the quality of its products, NCERT welcomes comments and suggestions which will enable us to undertake further revision and refinement. Director New Delhi National Council of Educational 20 December 2005 Research and Training Rationalised 2023-24 4 chemistry Rationalised 2023-24 answerS 5 Rationalisation of Content in the Textbook In view of the COVID-19 pandemic, it is imperative to reduce content load on students. The National Education Policy 2020, also emphasises reducing the content load and providing opportunities for experiential learning with creative mindset. In this background, the NCERT has undertaken the exercise to rationalise the textbooks across all classes. Learning Outcomes already developed by the NCERT across classes have been taken into consideration in this exercise. Contents of the textbooks have been rationalised in view of the following: • Overlapping with similar content included in other subject areas in the same class • Similar content included in the lower or higher class in the same subject • Difficulty level • Content, which is easily accessible to students without much interventions from teachers and can be learned by children through self-learning or peer-learning • Content, which is irrelevant in the present context This present edition, is a reformatted version after carrying out the changes given above. Rationalised 2023-24 6 chemistry Rationalised 2023-24 answerS 7 Textbook Development Committee Chairperson, Advisory Group for

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## Contents

redox reactions 235 Chemistry deals with varieties of matter and change of one kind of matter into the other. Transformation of matter from one kind into another occurs through the various types of reactions. One important category of such reactions is Redox Reactions. A number of phenomena, both physical as well as biological, are concerned with redox reactions. These reactions find extensive use in pharmaceutical, biological, industrial, metallurgical and agricultural areas. The importance of these reactions is apparent from the fact that burning of different types of fuels for obtaining energy for domestic, transport and other commercial purposes, electrochemical processes for extraction of highly reactive metals and non-metals, manufacturing of chemical compounds like caustic soda, operation of dry and wet batteries and corrosion of metals fall within the purview of redox processes. Of late, environmental issues like Hydrogen Economy (use of liquid hydrogen as fuel) and development of 'Ozone Hole' have started figuring under redox phenomenon. 7.1 CLASSICAL IDEA OF REDOX REACTIONS – OXIDATION AND REDUCTION REACTIONS Originally, the term oxidation was used to describe the addition of oxygen to an element or a compound. Because of the presence of dioxygen in the atmosphere (~20%), many elements combine with it and this is the principal reason why they commonly occur on the earth in the form of their oxides. The following reactions represent oxidation processes according to the limited definition of oxidation: 2 Mg (s) + O2 (g) → 2 MgO (s) (7.1) S (s) + O2 (g) → SO2 (g) (7.2) After studying this unit you will be able to • identify redox reactions as a class of reactions in which oxidation and reduction reactions occur simultaneously; • define the terms oxidation, reduction, oxidant (oxidising agent) and reductant (reducing agent); • explain mechanism of redox reactions by electron transfer process; • use the concept of oxidation number to identify oxidant and reductant in a reaction; • classify redox reaction into combination (synthesis), decomposition, displacement a n d d i s p r o p o r t i o n a t i o n reactions; • suggest a comparative order among various reductants and oxidants; • balance chemical equations using (i) oxidation number (ii) half reaction method; • learn the concept of redox reactions in terms of electrode processes. Unit 7 redox reactions Where there is oxidation, there is always reduction – Chemistry is essentially a study of redox systems. Rationalised 2023-24 236 chemistry In reactions (7.1) and (7.2), the elements magnesium and sulphur are oxidised on account of addition of oxygen to them. Similarly, methane is oxidised owing to the addition of oxygen to it. CH4 (g) + 2O2 (g) → CO2 (g) + 2H2O (l) (7.3) A careful examination of reaction (7.3) in which hydrogen has been replaced by oxygen prompted chemists to reinterpret oxidation in terms of removal of hydrogen from it and, therefore, the scope of term oxidation was broadened to include the removal of hydrogen from a substance. The following illustration is another reaction where removal of hydrogen can also be cited as an oxidation reaction. 2 H2S(g) + O2 (g) → 2 S (s) + 2 H2O (l) (7.4) As knowledge of chemists grew, it was natural to extend the term oxidation for reactions similar to (7.1 to 7.4), which do not involve oxygen but other electronegative elements. The oxidation of magnesium with fluorine, chlorine and sulphur etc. occurs according to the following reactions : Mg (s) + F2 (g) → MgF2 (s) (7.5) Mg (s) + Cl2 (g) → MgCl2 (s) (7.6) Mg (s) + S (s) → MgS (s) (7.7) Incorporating the reactions (7.5 to 7.7) within the fold of oxidation reactions encouraged chemists to consider not only the removal of hydrogen as oxidation, but also the removal of electropositive elements as oxidation. Thus the reaction : 2K4 [Fe(CN)6](aq) + H2O2 (aq) →2K3[Fe(CN)6](aq) + 2 KOH

(aq) is interpreted as oxidation due to the removal of electropositive element potassium from potassium ferrocyanide before it changes to potassium ferricyanide. To summarise, the term "oxidation" is defined as the addition of oxygen/electronegative element to a substance or removal of hydrogen/ electropositive element from a substance. In the beginning, reduction was considered as removal of oxygen from a compound. However, the term reduction has been broadened these days to include removal of oxygen/electronegative element from a substance or addition of hydrogen/ electropositive element to a substance. According to the definition given above, the following are the examples of reduction processes: 2 HgO (s) 2 Hg (l) + O2 (g) (7.8) (removal of oxygen from mercuric oxide ) 2 FeCl3 (aq) + H2 (g) →2 FeCl2 (aq) + 2 HCl(aq) (7.9) (removal of electronegative element, chlorine from ferric chloride) CH2 = CH2 (g) + H2 (g) → H3C – CH3 (g) (7.10) (addition of hydrogen) 2HgCl2 (aq) + SnCl2 (aq) → Hg2Cl2 (s)+SnCl4 (aq) (7.11) (addition of mercury to mercuric chloride) In reaction (7.11) simultaneous oxidation of stannous chloride to stannic chloride is also occurring because of the addition of electronegative element chlorine to it. It was soon realised that oxidation and reduction always occur simultaneously (as will be apparent by re-examining all the equations given above), hence, the word "redox" was coined for this class of chemical reactions. Problem 7.1 In the reactions given below, identify the species undergoing oxidation and reduction: (i) H2S (g) + Cl2 (g) → 2 HCl (g) + S (s) (ii) 3Fe3O4 (s) + 8 Al (s) → 9 Fe (s) + 4Al2O3 (s) (iii) 2 Na (s) + H2 (g) → 2 NaH (s) Solution (i) H2S is oxidised because a more electronegative element, chlorine is added to hydrogen (or a more electropositive element, hydrogen has been removed from S). Chlorine is reduced due to addition of hydrogen to it. (ii) Aluminium is oxidised because oxygen is added to it. Ferrous ferric oxide Rationalised 2023-24 redox reactions 237 (Fe3O4) is reduced because oxygen has been removed from it. (iii) With the careful application of the concept of electronegativity only we may infer that sodium is oxidised and hydrogen is reduced. Reaction (iii) chosen here prompts us to think in terms of another way to define redox reactions. 7.2 REDOX REACTIONS IN TERMS OF ELECTRON TRANSFER REACTIONS We have already learnt that the reactions 2Na(s) + Cl2(g) → 2NaCl (s) (7.12) 4Na(s) + O2(g) → 2Na2O(s) (7.13) 2Na(s) + S(s) → Na2S(s) (7.14) are redox reactions because in each of these reactions sodium is oxidised due to the addition of either oxygen or more electronegative element to sodium. Simultaneously, chlorine, oxygen and sulphur are reduced because to each of these, the electropositive element sodium has been added. From our knowledge of chemical bonding we also know that sodium chloride, sodium oxide and sodium sulphide are ionic compounds and perhaps better written as Na+Cl– (s), (Na+) 2O2–(s), and (Na+) 2 S2–(s). Development of charges on the species produced suggests us to rewrite the reactions (7.12 to 7.14) in the following manner : For convenience, each of the above processes can be considered as two separate steps, one involving the loss of electrons and the other the gain of electrons. As an illustration, we may further elaborate one of these, say, the formation of sodium chloride. 2 Na(s) → 2 Na+(g) + 2e– Cl2(g) + 2e– → 2 Cl– (g) Each of the above steps is called a half reaction, which explicitly shows involvement of electrons. Sum of the half reactions gives the overall reaction : 2 Na(s) + Cl2 (g) → 2 Na+ Cl– (s) or 2 NaCl (s) Reactions 7.12 to 7.14 suggest that half reactions that involve loss of electrons are called oxidation reactions. Similarly, the half reactions that involve gain of electrons are called reduction reactions. It may not be out of context to mention here that the new way of defining oxidation and reduction has been achieved only by establishing a correlation between the behaviour of species as per the classical idea and their interplay in electron-transfer change. In reactions (7.12 to 7.14) sodium, which is oxidised, acts as a reducing agent because it donates electron to each of the elements interacting with it and thus helps in reducing them. Chlorine, oxygen and sulphur are reduced and act as oxidising agents because these accept electrons from sodium. To summarise, we may mention that Oxidation : Loss of electron(s) by any species. Reduction : Gain of electron(s) by any species. Oxidising agent : Acceptor of electron(s). Reducing agent : Donor of electron(s). Problem 7.2 Justify

that the reaction: $2 Na(s) + H_2(g) \rightarrow 2 NaH (s)$ is a redox change. Solution Since in the above reaction the compound formed is an ionic compound, which may also be represented as $Na^+H^-$ (s), this suggests that one half reaction in this process is : $2 Na (s) \rightarrow 2 Na^+(g) + 2e^-$ Rationalised 2023-24 238 chemistry and the other half reaction is: $H_2 (g) + 2e^- \rightarrow 2 H^- (g)$ This splitting of the reaction under examination into two half reactions automatically reveals that here sodium is oxidised and hydrogen is reduced, therefore, the complete reaction is a redox change. 7.2.1 Competitive Electron Transfer Reactions Place a strip of metallic zinc in an aqueous solution of copper nitrate as shown in Fig. 7.1, for about one hour. You may notice that the strip becomes coated with reddish metallic copper and the blue colour of the solution disappears. Formation of $Zn^{2+}$ ions among the products can easily be judged when the blue colour of the solution due to $Cu^{2+}$ has disappeared. If hydrogen sulphide gas is passed through the colourless solution containing $Zn^{2+}$ ions, appearance of white zinc sulphide, ZnS can be seen on making the solution alkaline with ammonia. The reaction between metallic zinc and the aqueous solution of copper nitrate is : $Zn(s) + Cu^{2+} (aq) \rightarrow Zn^{2+} (aq) + Cu(s)$ (7.15) In reaction (7.15), zinc has lost electrons to form $Zn^{2+}$ and, therefore, zinc is oxidised. Evidently, now if zinc is oxidised, releasing electrons, something must be reduced, accepting the electrons lost by zinc. Copper ion is reduced by gaining electrons from the zinc. Reaction (7.15) may be rewritten as : At this stage we may investigate the state of equilibrium for the reaction represented by equation (7.15). For this purpose, let us place a strip of metallic copper in a zinc sulphate solution. No visible reaction is noticed and attempt to detect the presence of $Cu^{2+}$ ions by passing $H_2S$ gas through the solution to produce the black colour of cupric sulphide, CuS, does not succeed. Cupric sulphide has such a low solubility that this is an extremely sensitive test; yet the amount of $Cu^{2+}$ formed cannot be detected. We thus conclude that the state of equilibrium for the reaction (7.15) greatly favours the products over the reactants. Let us extend electron transfer reaction now to copper metal and silver nitrate solution in water and arrange a set-up as shown in Fig. 7.2. The solution develops blue colour due to the formation of $Cu^{2+}$ ions on account of the reaction: Fig. 7.1 Redox reaction between zinc and aqueous solution of copper nitrate occurring in a beaker. (7.16) Here, Cu(s) is oxidised to $Cu^{2+}(aq)$ and $Ag^+(aq)$ is reduced to Ag(s). Equilibrium greatly favours the products $Cu^{2+}$ (aq) and Ag(s). By way of contrast, let us also compare the reaction of metallic cobalt placed in nickel sulphate solution. The reaction that occurs here is : (7.17) Rationalised 2023-24 redox reactions 239 Fig. 7.2 Redox reaction between copper and aqueous solution of silver nitrate occurring in a beaker. At equilibrium, chemical tests reveal that both $Ni^{2+}(aq)$ and $Co^{2+}(aq)$ are present at moderate concentrations. In this case, neither the reactants [Co(s) and $Ni^{2+}(aq)$] nor the products [$Co^{2+}(aq)$ and Ni (s)] are greatly favoured. This competition for release of electrons incidently reminds us of the competition for release of protons among acids. The similarity suggests that we might develop a table in which metals and their ions are listed on the basis of their tendency to release electrons just as we do in the case of acids to indicate the strength of the acids. As a matter of fact we have already made certain comparisons. By comparison we have come to know that zinc releases electrons to copper and copper releases electrons to silver and, therefore, the electron releasing tendency of the metals is in the order: Zn>Cu>Ag. We would love to make our list more vast and design a metal activity series or electrochemical series. The competition for electrons between various metals helps us to design a class of cells, named as Galvanic cells in which the chemical reactions become the source of electrical energy. We would study more about these cells in Class XII. 7.3 OXIDATION NUMBER A less obvious example of electron transfer is realised when hydrogen combines with oxygen to form water by the reaction: $2H_2(g) + O_2 (g) \rightarrow 2H_2O (l)$ (7.18) Though not simple in its approach, yet we can visualise the H atom as going from a neutral (zero) state in $H_2$ to a positive state in $H_2O$, the O atom goes from a zero state in $O_2$ to a dinegative state in $H_2O$. It is assumed that there is an electron transfer from H to O and consequently $H_2$ is oxidised and $O_2$ is reduced. However, as we shall see later, the charge transfer is only partial and is perhaps better described as an electron shift rather

than a complete loss of electron by H and gain by O. What has been said here with respect to equation (7.18) may be true for a good number of other reactions involving covalent compounds. Two such examples of this class of the reactions are: $H_2(s) + Cl_2(g) \rightarrow 2HCl(g)$ (7.19) and, $CH_4(g) + 4Cl_2(g) \rightarrow CCl_4(l) + 4HCl(g)$ (7.20) In order to keep track of electron shifts in chemical reactions involving formation of covalent compounds, a more practical method of using oxidation number has been developed. In this method, it is always assumed that there is a complete transfer of electron from a less electronegative atom to a more electonegative atom. For example, we rewrite equations (7.18 to 7.20) to show charge on each of the atoms forming part of the reaction : 0 0 +1 −2 $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$ (7.21) 0 0 +1 −1 $H_2(s) + Cl_2(g) \rightarrow 2HCl(g)$ (7.22) −4 +1 0 +4 −1 +1 −1 $CH_4(g) + 4Cl_2(g) \rightarrow CCl_4(l) + 4HCl(g)$ (7.23) It may be emphasised that the assumption of electron transfer is made for book-keeping purpose only and it will become obvious at a later stage in this unit that it leads to the simple description of redox reactions. Oxidation number denotes the oxidation state of an element in a compound ascertained according to a set of rules formulated on the basis that electron pair Rationalised 2023-24 240 chemistry in a covalent bond belongs entirely to more electronegative element. It is not always possible to remember or make out easily in a compound/ion, which element is more electronegative than the other. Therefore, a set of rules has been formulated to determine the oxidation number of an element in a compound/ion. If two or more than two atoms of an element are present in the molecule/ion such as $Na_2S_2O_3$/$Cr_2O_7^{2-}$, the oxidation number of the atom of that element will then be the average of the oxidation number of all the atoms of that element. We may at this stage, state the rules for the calculation of oxidation number. These rules are: 1. In elements, in the free or the uncombined state, each atom bears an oxidation number of zero. Evidently each atom in $H_2$, $O_2$, $Cl_2$, $O_3$, $P_4$, $S_8$, Na, Mg, Al has the oxidation number zero. 2. For ions composed of only one atom, the oxidation number is equal to the charge on the ion. Thus $Na^+$ ion has an oxidation number of +1, $Mg^{2+}$ ion, +2, $Fe^{3+}$ ion, +3, $Cl^-$ ion, −1, $O^{2-}$ ion, −2; and so on. In their compounds all alkali metals have oxidation number of +1, and all alkaline earth metals have an oxidation number of +2. Aluminium is regarded to have an oxidation number of +3 in all its compounds. 3. The oxidation number of oxygen in most compounds is −2. However, we come across two kinds of exceptions here. One arises in the case of peroxides and superoxides, the compounds of oxygen in which oxygen atoms are directly linked to each other. While in peroxides (e.g., $H_2O_2$, $Na_2O_2$), each oxygen atom is assigned an oxidation number of −1, in superoxides (e.g., $KO_2$, $RbO_2$) each oxygen atom is assigned an oxidation number of −(½). The second exception appears rarely, i.e. when oxygen is bonded to fluorine. In such compounds e.g., oxygen difluoride ($OF_2$) and dioxygen difluoride ($O_2F_2$), the oxygen is assigned an oxidation number of +2 and +1, respectively. The number assigned to oxygen will depend upon the bonding state of oxygen but this number would now be a positive figure only. 4. The oxidation number of hydrogen is +1, except when it is bonded to metals in binary compounds (that is compounds containing two elements). For example, in LiH, NaH, and $CaH_2$, its oxidation number is −1. 5. In all its compounds, fluorine has an oxidation number of −1. Other halogens (Cl, Br, and I) also have an oxidation number of −1, when they occur as halide ions in their compounds. Chlorine, bromine and iodine when combined with oxygen, for example in oxoacids and oxoanions, have positive oxidation numbers. 6. The algebraic sum of the oxidation number of all the atoms in a compound must be zero. In polyatomic ion, the algebraic sum of all the oxidation numbers of atoms of the ion must equal the charge on the ion. Thus, the sum of oxidation number of three oxygen atoms and one carbon atom in the carbonate ion, $(CO_3)^{2-}$ must equal −2. By the application of above rules, we can find out the oxidation number of the desired element in a molecule or in an ion. It is clear that the metallic elements have positive oxidation number and nonmetallic elements have positive or negative oxidation number. The atoms of transition elements usually display several positive oxidation states. The highest oxidation number of a representative element is the group number for the first two groups and the group number minus 10 (following the

long form of periodic table) for the other groups. Thus, it implies that the highest value of oxidation number exhibited by an atom of an element generally increases across the period in the periodic table. In the third period, the highest value of oxidation number changes from 1 to 7 as indicated below in the compounds of the elements. A term that is often used interchangeably with the oxidation number is the oxidation state. Thus in $CO_2$, the oxidation state of carbon is +4, that is also its oxidation number and similarly the oxidation state as well as oxidation number of oxygen is – 2. This implies that the oxidation number denotes the oxidation state of an element in a compound.

The oxidation number/state of a metal in a compound is sometimes presented according to the notation given by German chemist, Alfred Stock. It is popularly known as Stock notation. According to this, the oxidation number is expressed by putting a Roman numeral representing the oxidation number in parenthesis after the symbol of the metal in the molecular formula. Thus aurous chloride and auric chloride are written as Au(I)Cl and Au(III)Cl3. Similarly, stannous chloride and stannic chloride are written as Sn(II)Cl2 and Sn(IV)Cl4. This change in oxidation number implies change in oxidation state, which in turn helps to identify whether the species is present in oxidised form or reduced form. Thus, Hg2(I)Cl2 is the reduced form of Hg(II) Cl2.

**Problem 7.3** Using Stock notation, represent the following compounds : HAuCl4, Tl2O, FeO, Fe2O3, CuI, CuO, MnO and MnO2. **Solution** By applying various rules of calculating the oxidation number of the desired element in a compound, the oxidation number of each metallic element in its compound is as follows: HAuCl4 → Au has 3 Tl2O → Tl has 1 FeO → Fe has 2 Fe2O3 → Fe has 3 CuI → Cu has 1 CuO → Cu has 2 MnO → Mn has 2 MnO2 → Mn has 4 Therefore, these compounds may be represented as: HAu(III)Cl4, Tl2(I)O, Fe(II)O, Fe2(III)O3, Cu(I)I, Cu(II)O, Mn(II)O, Mn(IV)O2. The idea of oxidation number has been invariably applied to define oxidation, reduction, oxidising agent (oxidant), reducing agent (reductant) and the redox reaction. To summarise, we may say that:

Oxidation: An increase in the oxidation number of the element in the given substance. Reduction : A decrease in the oxidation number of the element in the given substance. Oxidising agent: A reagent which can increase the oxidation number of an element in a given substance. These reagents are called as oxidants also. Reducing agent: A reagent which lowers the oxidation number of an element in a given substance. These reagents are also called as reductants. Redox reactions: Reactions which involve change in oxidation number of the interacting species. **Problem 7.4** Justify that the reaction: 2Cu2O(s) + Cu2S(s) → 6Cu(s) + SO2(g) is a redox reaction. Identify the species oxidised/reduced, which acts as an oxidant and which acts as a reductant. **Solution** Let us assign oxidation number to each of the species in the reaction under examination. This results into: +1 −2 +1 −2 0 +4 −2 2Cu2O(s) + Cu2S(s) → 6Cu(s) + SO2 We therefore, conclude that in this reaction copper is reduced from +1 state to zero oxidation state and sulphur is oxidised from –2 state to +4 state. The above reaction is thus a redox reaction.

| Group | 1 | 2 | 13 | 14 | 15 | 16 | 17 |
|---|---|---|---|---|---|---|---|
| Element | Na | Mg | Al | Si | P | S | Cl |
| Compound | NaCl | MgSO4 | AlF3 | SiCl4 | P4O10 | SF6 | HClO |
| Highest oxidation number state of the group element | +1 | +2 | +3 | +4 | +5 | +6 | +7 |

Further, Cu2O helps sulphur in Cu2S to increase its oxidation number, therefore, Cu(I) is an oxidant; and sulphur of Cu2S helps copper both in Cu2S itself and Cu2O to decrease its oxidation number; therefore, sulphur of Cu2S is reductant. **7.3.1 Types of Redox Reactions** 1. Combination reactions A combination reaction may be denoted in the manner: A + B → C Either A and B or both A and B must be in the elemental form for such a reaction to be a redox reaction. All combustion reactions, which make use of elemental dioxygen, as well as other reactions involving elements other than dioxygen, are redox reactions. Some important examples of this category are: 0 0 +4 −2 C(s) + O2 (g) CO2(g) (7.24) 0 0 +2 −3 3Mg(s) + N2(g) Mg3N2(s) (7.25) −4+1 0 +4 −2 +1 −2 CH4(g) + 2O2(g) CO2(g) + 2H2O (l) 2. Decomposition reactions Decomposition reactions are the opposite of combination reactions. Precisely, a decomposition reaction leads to the breakdown of a compound into two or more components at least one of which must be in the elemental state. Examples of this class of reactions are: +1 −2 0 0 2H2O (l) 2H2 (g) + O2(g) (7.26) +1 −

$1\ 0\ 0$ $2NaH\ (s)$ $2Na\ (s) + H_2(g)$ (7.27) $+1\ +5\ -2\ +1\ -1\ 0$ $2KClO_3\ (s)$ $2KCl\ (s) + 3O_2(g)$ (7.28) It may carefully be noted that there is no change in the oxidation number of hydrogen in methane under combination reactions and that of potassium in potassium chlorate in reaction (7.28). This may also be noted here that all decomposition reactions are not redox reactions. For example, decomposition of calcium carbonate is not a redox reaction. $+2\ +4\ -2\ +2\ -2\ +4\ -2$ $CaCO_3\ (s)$ $CaO(s) + CO_2(g)$ 3. Displacement reactions In a displacement reaction, an ion (or an atom) in a compound is replaced by an ion (or an atom) of another element. It may be denoted as: $X + YZ \rightarrow XZ + Y$ Displacement reactions fit into two categories: metal displacement and non-metal displacement. (a) Metal displacement: A metal in a compound can be displaced by another metal in the uncombined state. We have already discussed about this class of the reactions under section 7.2.1. Metal displacement reactions find many applications in metallurgical processes in which pure metals are obtained from their compounds in ores. A few such examples are: $+2\ +6\ -2\ 0\ 0\ +2\ +6\ -2$ $CuSO_4(aq) + Zn\ (s) \rightarrow Cu(s) + ZnSO_4\ (aq)$ (7.29) $+5\ -2\ 0\ 0\ +2\ -2$ $V_2O_5\ (s) + 5Ca\ (s)$ $2V\ (s) + 5CaO\ (s)$ (7.30) $+4\ -1\ 0\ 0\ +2\ -1$ $TiCl_4\ (l) + 2Mg\ (s)$ $Ti\ (s) + 2\ MgCl_2\ (s)$ (7.31) $+3\ -2\ 0\ +3\ -2\ 0$ $Cr_2O_3\ (s) + 2\ Al\ (s)$ $Al_2O_3\ (s) + 2Cr(s)$ (7.32) In each case, the reducing metal is a better reducing agent than the one that is being reduced which evidently shows more capability to lose electrons as compared to the one that is reduced. (b) Non-metal displacement: The nonmetal displacement redox reactions include hydrogen displacement and a rarely occurring reaction involving oxygen displacement. Rationalised 2023-24 redox reactions 243 All alkali metals and some alkaline earth metals (Ca, Sr, and Ba) which are very good reductants, will displace hydrogen from cold water. $0\ +1\ -2\ +1\ -2\ +1\ 0$ $2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$ (7.33) $0\ +1\ -2\ +2\ -2\ +1\ 0$ $Ca(s) + 2H_2O(l) \rightarrow Ca(OH)_2\ (aq) + H_2(g)$ (7.34) Less active metals such as magnesium and iron react with steam to produce dihydrogen gas: $0\ +1\ -2\ +2\ -2\ +1\ 0$ $Mg(s) + 2H_2O(l)$ $Mg(OH)_2(s) + H_2(g)$ (7.35) $0\ +1\ -2\ +3\ -2\ 0$ $2Fe(s) + 3H_2O(l)$ $Fe_2O_3(s) + 3H_2(g)$ (7.36) Many metals, including those which do not react with cold water, are capable of displacing hydrogen from acids. Dihydrogen from acids may even be produced by such metals which do not react with steam. Cadmium and tin are the examples of such metals. A few examples for the displacement of hydrogen from acids are: $0\ +1\ -1\ +2\ -1\ 0$ $Zn(s) + 2HCl(aq) \rightarrow ZnCl_2\ (aq) + H_2\ (g)$ (7.37) $0\ +1\ -1\ +2\ -1\ 0$ $Mg\ (s) + 2HCl\ (aq) \rightarrow MgCl_2\ (aq) + H_2\ (g)$ (7.38) $0\ +1\ -1\ +2\ -1\ 0$ $Fe(s) + 2HCl(aq) \rightarrow FeCl_2(aq) + H_2(g)$ (7.39) Reactions (7.37 to 7.39) are used to prepare dihydrogen gas in the laboratory. Here, the reactivity of metals is reflected in the rate of hydrogen gas evolution, which is the slowest for the least active metal Fe, and the fastest for the most reactive metal, Mg. Very less active metals, which may occur in the native state such as silver (Ag), and gold (Au) do not react even with hydrochloric acid. In section (7.2.1) we have already discussed that the metals – zinc (Zn), copper (Cu) and silver (Ag) through tendency to lose electrons show their reducing activity in the order Zn> Cu>Ag. Like metals, activity series also exists for the halogens. The power of these elements as oxidising agents decreases as we move down from fluorine to iodine in group 17 of the periodic table. This implies that fluorine is so reactive that it can replace chloride, bromide and iodide ions in solution. In fact, fluorine is so reactive that it attacks water and displaces the oxygen of water : $+1\ -2\ 0\ +1\ -1\ 0$ $2H_2O\ (l) + 2F_2\ (g) \rightarrow 4HF(aq) + O_2(g)$ (7.40) It is for this reason that the displacement reactions of chlorine, bromine and iodine using fluorine are not generally carried out in aqueous solution. On the other hand, chlorine can displace bromide and iodide ions in an aqueous solution as shown below: $0\ +1\ -1\ +1\ -1\ 0$ $Cl_2\ (g) + 2KBr\ (aq) \rightarrow 2\ KCl\ (aq) + Br_2\ (l)$ (7.41) $0\ +1\ -1\ +1\ -1\ 0$ $Cl_2\ (g) + 2KI\ (aq) \rightarrow 2\ KCl\ (aq) + I_2\ (s)$ (7.42) As $Br_2$ and $I_2$ are coloured and dissolve in $CCl_4$, can easily be identified from the colour of the solution. The above reactions can be written in ionic form as: $0\ -1\ -1\ 0$ $Cl_2\ (g) + 2Br^-\ (aq) \rightarrow 2Cl^-\ (aq) + Br_2\ (l)$ (7.41a) $0\ -1\ -1\ 0$ $Cl_2\ (g) + 2I^-\ (aq) \rightarrow 2Cl^-\ (aq) + I_2\ (s)$ (7.42b) Reactions (7.41) and (7.42) form the basis of identifying $Br^-$ and $I^-$ in the laboratory through the test popularly known as 'Layer Test'. It may not be out of place to mention here that bromine likewise can displace iodide ion in solution: $0\ -1\ -1\ 0$ $Br_2\ (l) + 2I^-\ (aq) \rightarrow 2Br^-\ (aq) + I_2\ (s)$ (7.43) The halogen displacement reactions have a direct

industrial application. The recovery of halogens from their halides requires an oxidation process, which is represented by: $2X^- \rightarrow X_2 + 2e^-$ (7.44) here X denotes a halogen element. Whereas chemical means are available to oxidise $Cl^-$, $Br^-$ and $I^-$, as fluorine is the strongest oxidising Rationalised 2023-24 244 chemistry agent; there is no way to convert $F^-$ ions to $F_2$ by chemical means. The only way to achieve $F_2$ from $F^-$ is to oxidise electrolytically, the details of which you will study at a later stage. 4. Disproportionation reactions Disproportionation reactions are a special type of redox reactions. In a disproportionation reaction an element in one oxidation state is simultaneously oxidised and reduced. One of the reacting substances in a disproportionation reaction always contains an element that can exist in at least three oxidation states. The element in the form of reacting substance is in the intermediate oxidation state; and both higher and lower oxidation states of that element are formed in the reaction. The decomposition of hydrogen peroxide is a familiar example of the reaction, where oxygen experiences disproportionation. $+1\ -1\ +1\ -2\ 0$
$2H_2O_2$ (aq) $\rightarrow 2H_2O$(l) + $O_2$(g) (7.45) Here the oxygen of peroxide, which is present in $-1$ state, is converted to zero oxidation state in $O_2$ and decreases to $-2$ oxidation state in $H_2O$. Phosphorous, sulphur and chlorine undergo disproportionation in the alkaline medium as shown below : $0\ -3\ +1$
$P_4$(s) + $3OH^-$ (aq)+ $3H_2O$(l) $\rightarrow PH_3$(g) + $3H_2PO_2^-$ (aq) (7.46) $0\ -2\ +2$ $S_8$(s) + 12 $OH^-$ (aq) $\rightarrow 4S^{2-}$ (aq) + $2S_2O_3^{2-}$(aq) + $6H_2O$(l) (7.47) $0\ +1\ -1$ $Cl_2$ (g) + 2 $OH^-$ (aq) $\rightarrow ClO^-$ (aq) + $Cl^-$ (aq) + $H_2O$ (l) (7.48) The reaction (7.48) describes the formation of household bleaching agents. The hypochlorite ion ($ClO^-$) formed in the reaction oxidises the colour-bearing stains of the substances to colourless compounds. It is of interest to mention here that whereas bromine and iodine follow the same trend as exhibited by chlorine in reaction (7.48), fluorine shows deviation from this behaviour when it reacts with alkali. The reaction that takes place in the case of fluorine is as follows: 2 $F_2$(g) + $2OH^-$ (aq) $\rightarrow$ 2 $F^-$ (aq) + $OF_2$(g) + $H_2O$(l) (7.49) (It is to be noted with care that fluorine in reaction (7.49) will undoubtedly attack water to produce some oxygen also). This departure shown by fluorine is not surprising for us as we know the limitation of fluorine that, being the most electronegative element, it cannot exhibit any positive oxidation state. This means that among halogens, fluorine does not show a disproportionation tendency. Problem 7.5 Which of the following species, do not show disproportionation reaction and why ? $ClO^-$, $ClO_2^-$, $ClO_3^-$ and $ClO_4^-$ Also write reaction for each of the species that disproportionates. Solution Among the oxoanions of chlorine listed above, $ClO_4^-$ does not disproportionate because in this oxoanion chlorine is present in its highest oxidation state that is, $+7$. The disproportionation reactions for the other three oxoanions of chlorine are as follows: $+1\ -1\ +5\ 3ClO^- \rightarrow 2Cl^- + ClO_3^-\ +3\ +5\ -1\ 6\ ClO_2^- \rightarrow 4ClO_3^- + 2Cl^-\ +5\ -1\ +7\ 4ClO_3^- \rightarrow Cl^- + 3\ ClO_4^-$ Problem 7.6 Suggest a scheme of classification of the following redox reactions (a) $N_2$ (g) + $O_2$ (g) $\rightarrow$ 2 NO (g) (b) $2Pb(NO_3)_2$(s) $\rightarrow 2PbO$(s) + 4 $NO_2$ (g) + $O_2$ (g) (c) NaH(s) + $H_2O$(l) $\rightarrow$ NaOH(aq) + $H_2$ (g) (d) $2NO_2$(g) + $2OH^-$ (aq) $\rightarrow NO_2^-$ (aq) + $NO_3^-$ (aq)+$H_2O$(l) Rationalised 2023-24 redox reactions 245 Solution In reaction (a), the compound nitric oxide is formed by the combination of the elemental substances, nitrogen and oxygen; therefore, this is an example of combination redox reactions. The reaction (b) involves the breaking down of lead nitrate into three components; therefore, this is categorised under decomposition redox reaction. In The Paradox of Fractional Oxidation Number Sometimes, we come across with certain compounds in which the oxidation number of a particular element in the compound is in fraction. Examples are: $C_3O_2$ [where oxidation number of carbon is (4/3)], $Br_3O_8$ [where oxidation number of bromine is (16/3)] and $Na_2S_4O_6$ (where oxidation number of sulphur is 2.5). We know that the idea of fractional oxidation number is unconvincing to us, because electrons are never shared/transferred in fraction. Actually this fractional oxidation state is the average oxidation state of the element under examination and the structural parameters reveal that the element for whom fractional oxidation state is realised is present in different oxidation states. Structure of the species $C_3O_2$, $Br_3O_8$ and $S_4O_6^{2-}$ reveal the following bonding situations: $+2\ 0\ +2$ O = C = C* = C = O Structure of $C_3O_2$ (carbon suboxide)

Structure of Br3O8 (tribromooctaoxide) Structure of S4O6 2– (tetrathionate ion) The element marked with asterisk in each species is exhibiting the different oxidation state (oxidation number) from rest of the atoms of the same element in each of the species. This reveals that in C3O2, two carbon atoms are present in +2 oxidation state each, whereas the third one is present in zero oxidation state and the average is 4/3. However, the realistic picture is +2 for two terminal carbons and zero for the middle carbon. Likewise in Br3O8, each of the two terminal bromine atoms are present in +6 oxidation state and the middle bromine is present in +4 oxidation state. Once again the average, that is different from reality, is 16/3. In the same fashion, in the species S4O6 2–, each of the two extreme sulphurs exhibits oxidation state of +5 and the two middle sulphurs as zero. The average of four oxidation numbers of sulphurs of the S4O6 2– is 2.5, whereas the reality being + 5,0,0 and +5 oxidation number respectively for each sulphur. We may thus, in general, conclude that the idea of fractional oxidation state should be taken with care and the reality is revealed by the structures only. Further, whenever we come across with fractional oxidation state of any particular element in any species, we must understand that this is the average oxidation number only. In reality (revealed by structures only), the element in that particular species is present in more than one whole number oxidation states. Fe3O4, Mn3O4, Pb3O4 are some of the other examples of the compounds, which are mixed oxides, where we come across with fractional oxidation states of the metal atom. However, the oxidation states may be in fraction as in O2 + and O2 – where it is +½ and –½ respectively. reaction (c), hydrogen of water has been displaced by hydride ion into dihydrogen gas. Therefore, this may be called as displacement redox reaction. The reaction (d) involves disproportionation of NO2 (+4 state) into NO2 – (+3 state) and NO3 – (+5 state). Therefore reaction (d) is an example of disproportionation redox reaction. Rationalised 2023-24 246 chemistry Problem 7.8 Write the net ionic equation for the reaction of potassium dichromate(VI), K2Cr2O7 with sodium sulphite, Na2SO3, in an acid solution to give chromium(III) ion and the sulphate ion. Problem 7.7 Why do the following reactions proceed differently ? Pb3O4 + 8HCl → 3PbCl2 + Cl2 + 4H2O and Pb3O4 + 4HNO3 → 2Pb(NO3) 2 + PbO2 + 2H2O Solution Pb3O4 is actually a stoichiometric mixture of 2 mol of PbO and 1 mol of PbO2. In PbO2, lead is present in +4 oxidation state, whereas the stable oxidation state of lead in PbO is +2. PbO2 thus can act as an oxidant (oxidising agent) and, therefore, can oxidise Cl– ion of HCl into chlorine. We may also keep in mind that PbO is a basic oxide. Therefore, the reaction Pb3O4 + 8HCl → 3PbCl2 + Cl2 + 4H2O can be splitted into two reactions namely: 2PbO + 4HCl → 2PbCl2 + 2H2O (acid-base reaction) +4 –1 +2 0 PbO2 + 4HCl → PbCl2 + Cl2 +2H2O (redox reaction) Since HNO3 itself is an oxidising agent therefore, it is unlikely that the reaction may occur between PbO2 and HNO3. However, the acid-base reaction occurs between PbO and HNO3 as: 2PbO + 4HNO3 → 2Pb(NO3) 2 + 2H2O It is the passive nature of PbO2 against HNO3 that makes the reaction different from the one that follows with HCl. (a) Oxidation Number Method: In writing equations for oxidation-reduction reactions, just as for other reactions, the compositions and formulas must be known for the substances that react and for the products that are formed. The oxidation number method is now best illustrated in the following steps: Step 1: Write the correct formula for each reactant and product. Step 2: Identify atoms which undergo change in oxidation number in the reaction by assigning the oxidation number to all elements in the reaction. Step 3: Calculate the increase or decrease in the oxidation number per atom and for the entire molecule/ion in which it occurs. If these are not equal then multiply by suitable number so that these become equal. (If you realise that two substances are reduced and nothing is oxidised or vice-versa, something is wrong. Either the formulas of reactants or products are wrong or the oxidation numbers have not been assigned properly). Step 4: Ascertain the involvement of ions if the reaction is taking place in water, add H+ or OH– ions to the expression on the appropriate side so that the total ionic charges of reactants and products are equal. If the reaction is carried out in acidic solution, use H+ ions in the equation; if in basic solution, use OH– ions. Step 5 : Make the numbers of

hydrogen atoms in the expression on the two sides equal by adding water ($H_2O$) molecules to the reactants or products. Now, also check the number of oxygen atoms. If there are the same number of oxygen atoms in the reactants and products, the equation then represents the balanced redox reaction. Let us now explain the steps involved in the method with the help of a few problems given below: 7.3.2 Balancing of Redox Reactions Two methods are used to balance chemical equations for redox processes. One of these methods is based on the change in the oxidation number of reducing agent and the oxidising agent and the other method is based on splitting the redox reaction into two half reactions — one involving oxidation and the other involving reduction. Both these methods are in use and the choice of their use rests with the individual using them. Rationalised 2023-24 redox reactions 247 Solution Step 1: The skeletal ionic equation is: $Cr_2O_7^{2-}(aq) + SO_3^{2-}(aq) \rightarrow Cr^{3+}(aq) + SO_4^{2-}(aq)$ Step 2: Assign oxidation numbers for Cr and S +6 −2 +4 −2 +3 +6 −2 $Cr_2O_7^{2-}(aq) + SO_3^{2-}(aq) \rightarrow Cr(aq)+SO_4^{2-}(aq)$ This indicates that the dichromate ion is the oxidant and the sulphite ion is the reductant. Step 3: Calculate the increase and decrease of oxidation number, and make them equal: from step-2 we can notice that there is change in oxidation state of chromium and sulphur. Oxidation state of chromium changes form +6 to +3. There is decrease of +3 in oxidation state of chromium on right hand side of the equation. Oxidation state of sulphur changes from +4 to +6. There is an increase of +2 in the oxidation state of sulphur on right hand side. To make the increase and decrease of oxidation state equal, place numeral 2 before cromium ion on right hand side and numeral 3 before sulphate ion on right hand side and balance the chromium and sulphur atoms on both the sides of the equation. Thus we get +6 −2 +4 −2 +3 $Cr_2O_7^{2-}(aq) + 3SO_3^{2-}(aq) \rightarrow 2Cr^{3+}(aq) +$ +6 −2 $3SO_4^{2-}(aq)$ Step 4: As the reaction occurs in the acidic medium, and further the ionic charges are not equal on both the sides, add $8H^+$ on the left to make ionic charges equal $Cr_2O_7^{2-}(aq) + 3SO_3^{2-}(aq)+ 8H^+ \rightarrow 2Cr^{3+}(aq) + 3SO_4^{2-}(aq)$ Step 5: Finally, count the hydrogen atoms, and add appropriate number of water molecules (i.e., $4H_2O$) on the right to achieve balanced redox change. $Cr_2O_7^{2-}(aq) + 3SO_3^{2-}(aq)+ 8H^+(aq) \rightarrow 2Cr^{3+}(aq) + 3SO_4^{2-}(aq) +4H_2O(l)$ Problem 7.9 Permanganate ion reacts with bromide ion in basic medium to give manganese dioxide and bromate ion. Write the balanced ionic equation for the reaction. Solution Step 1: The skeletal ionic equation is : $MnO_4^-(aq) + Br^-(aq) \rightarrow MnO_2(s) + BrO_3^-(aq)$ Step 2: Assign oxidation numbers for Mn and Br +7 −1 +4 +5 $MnO_4^-(aq) + Br^-(aq) \rightarrow MnO_2(s) + BrO_3^-(aq)$ this indicates that permanganate ion is the oxidant and bromide ion is the reductant. Step 3: Calculate the increase and decrease of oxidation number, and make the increase equal to the decrease. +7 −1 +4 +5 $2MnO_4^-(aq)+Br^-(aq) \rightarrow 2MnO_2(s)+BrO_3^-(aq)$ Step 4: As the reaction occurs in the basic medium, and the ionic charges are not equal on both sides, add $2OH^-$ ions on the right to make ionic charges equal. $2MnO_4^-(aq) + Br^-(aq) \rightarrow 2MnO_2(s) + BrO_3^-(aq) + 2OH^-(aq)$ Step 5: Finally, count the hydrogen atoms and add appropriate number of water molecules (i.e. one $H_2O$ molecule) on the left side to achieve balanced redox change. $2MnO_4^-(aq) + Br^-(aq) + H_2O(l) \rightarrow 2MnO_2(s) + BrO_3^-(aq) + 2OH^-(aq)$ (b) Half Reaction Method: In this method, the two half equations are balanced separately and then added together to give balanced equation. Suppose we are to balance the equation showing the oxidation of $Fe^{2+}$ ions to $Fe^{3+}$ ions by dichromate ions $(Cr_2O_7)^{2-}$ in acidic medium, wherein, $Cr_2O_7^{2-}$ ions are reduced to $Cr^{3+}$ ions. The following steps are involved in this task. Step 1: Produce unbalanced equation for the reaction in ionic form : $Fe^{2+}(aq) + Cr_2O_7^{2-}(aq) \rightarrow Fe^{3+}(aq) + Cr^{3+}(aq)$ (7.50) Rationalised 2023-24 248 chemistry Step 2: Separate the equation into halfreactions: +2 +3 Oxidation half : $Fe^{2+}(aq) \rightarrow Fe^{3+}(aq)$ (7.51) +6 −2 +3 Reduction half : $Cr_2O_7^{2-}(aq) \rightarrow Cr^{3+}(aq)$ (7.52) Step 3: Balance the atoms other than O and H in each half reaction individually. Here the oxidation half reaction is already balanced with respect to Fe atoms. For the reduction half reaction, we multiply the $Cr^{3+}$ by 2 to balance Cr atoms. $Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq)$ (7.53) Step 4: For reactions occurring in acidic medium, add $H_2O$ to balance O atoms and $H^+$ to balance H atoms. Thus, we get : $Cr_2O_7^{2-}(aq) + 14H^+(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$ (7.54) Step 5: Add electrons to one side of the half reaction

to balance the charges. If need be, make the number of electrons equal in the two half reactions by multiplying one or both half reactions by appropriate number. The oxidation half reaction is thus rewritten to balance the charge:

$$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^- \quad (7.55)$$

Now in the reduction half reaction there are net twelve positive charges on the left hand side and only six positive charges on the right hand side. Therefore, we add six electrons on the left side.

$$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l) \quad (7.56)$$

To equalise the number of electrons in both the half reactions, we multiply the oxidation half reaction by 6 and write as:

$$6Fe^{2+}(aq) \rightarrow 6Fe^{3+}(aq) + 6e^- \quad (7.57)$$

Step 6: We add the two half reactions to achieve the overall reaction and cancel the electrons on each side. This gives the net ionic equation as:

$$6Fe^{2+}(aq) + Cr_2O_7^{2-}(aq) + 14H^+(aq) \rightarrow 6Fe^{3+}(aq) + 2Cr^{3+}(aq) + 7H_2O(l) \quad (7.58)$$

Step 7: Verify that the equation contains the same type and number of atoms and the same charges on both sides of the equation. This last check reveals that the equation is fully balanced with respect to number of atoms and the charges.

For the reaction in a basic medium, first balance the atoms as is done in acidic medium. Then for each $H^+$ ion, add an equal number of $OH^-$ ions to both sides of the equation. Where $H^+$ and $OH^-$ appear on the same side of the equation, combine these to give $H_2O$.

**Problem 7.10** Permanganate(VII) ion, $MnO_4^-$ in basic solution oxidises iodide ion, $I^-$ to produce molecular iodine ($I_2$) and manganese (IV) oxide ($MnO_2$). Write a balanced ionic equation to represent this redox reaction.

**Solution**
Step 1: First we write the skeletal ionic equation, which is

$$MnO_4^-(aq) + I^-(aq) \rightarrow MnO_2(s) + I_2(s)$$

Step 2: The two half-reactions are:

Oxidation half : $\overset{-1}{I^-}(aq) \rightarrow \overset{0}{I_2}(s)$

Reduction half: $\overset{+7}{Mn}O_4^-(aq) \rightarrow \overset{+4}{Mn}O_2(s)$

Step 3: To balance the I atoms in the oxidation half reaction, we rewrite it as:

$$2I^-(aq) \rightarrow I_2(s)$$

Step 4: To balance the O atoms in the reduction half reaction, we add two water molecules on the right:

$$MnO_4^-(aq) \rightarrow MnO_2(s) + 2H_2O(l)$$

To balance the H atoms, we add four $H^+$ ions on the left:

$$MnO_4^-(aq) + 4H^+(aq) \rightarrow MnO_2(s) + 2H_2O(l)$$

As the reaction takes place in a basic solution, therefore, for four $H^+$ ions, we add four $OH^-$ ions to both sides of the equation:

$$MnO_4^-(aq) + 4H^+(aq) + 4OH^-(aq) \rightarrow MnO_2(s) + 2H_2O(l) + 4OH^-(aq)$$

Replacing the $H^+$ and $OH^-$ ions with water, Rationalised 2023-24 redox reactions 249 the resultant equation is:

$$MnO_4^-(aq) + 2H_2O(l) \rightarrow MnO_2(s) + 4OH^-(aq)$$

Step 5 : In this step we balance the charges of the two half-reactions in the manner depicted as:

$$2I^-(aq) \rightarrow I_2(s) + 2e^-$$
$$MnO_4^-(aq) + 2H_2O(l) + 3e^- \rightarrow MnO_2(s) + 4OH^-(aq)$$

Now to equalise the number of electrons, we multiply the oxidation half-reaction by 3 and the reduction half-reaction by 2.

$$6I^-(aq) \rightarrow 3I_2(s) + 6e^-$$
$$2MnO_4^-(aq) + 4H_2O(l) + 6e^- \rightarrow 2MnO_2(s) + 8OH^-(aq)$$

Step 6: Add two half-reactions to obtain the net reactions after cancelling electrons on both sides.

$$6I^-(aq) + 2MnO_4^-(aq) + 4H_2O(l) \rightarrow 3I_2(s) + 2MnO_2(s) + 8OH^-(aq)$$

Step 7: A final verification shows that the equation is balanced in respect of the number of atoms and charges on both sides.

**7.3.3 Redox Reactions as the Basis for Titrations**

In acid-base systems we come across with a titration method for finding out the strength of one solution against the other using a pH sensitive indicator. Similarly, in redox systems, the titration method can be adopted to determine the strength of a reductant/ oxidant using a redox sensitive indicator. The usage of indicators in redox titration is illustrated below:

(i) In one situation, the reagent itself is intensely coloured, e.g., permanganate ion, $MnO_4^-$. Here $MnO_4^-$ acts as the self indicator. The visible end point in this case is achieved after the last of the reductant ($Fe^{2+}$ or $C_2O_4^{2-}$) is oxidised and the first lasting tinge of pink colour appears at $MnO_4^-$ concentration as low as $10^{-6}$ mol dm$^{-3}$ ($10^{-6}$ mol L$^{-1}$). This ensures a minimal 'overshoot' in colour beyond the equivalence point, the point where the reductant and the oxidant are equal in terms of their mole stoichiometry.

(ii) If there is no dramatic auto-colour change (as with $MnO_4^-$ titration), there are indicators which are oxidised immediately after the last bit of the reactant is consumed, producing a dramatic colour change. The best example is afforded by $Cr_2O_7^{2-}$, which is not a self-indicator, but oxidises the indicator substance diphenylamine just after the equivalence point to produce an intense blue colour, thus signalling the end point.

(iii) There is yet another method which is interesting and quite common. Its use is restricted to those reagents which are able to oxidise $I^-$ ions,

say, for example, Cu(II): $2Cu^{2+}(aq) + 4I^-(aq) \rightarrow Cu_2I_2(s) + I_2(aq)$ (7.59) This method relies on the facts that iodine itself gives an intense blue colour with starch and has a very specific reaction with thiosulphate ions ($S_2O_3^{2-}$), which too is a redox reaction: $I_2(aq) + 2 S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$ (7.60) $I_2$, though insoluble in water, remains in solution containing KI as $KI_3$. On addition of starch after the liberation of iodine from the reaction of $Cu^{2+}$ ions on iodide ions, an intense blue colour appears. This colour disappears as soon as the iodine is consumed by the thiosulphate ions. Thus, the end-point can easily be tracked and the rest is the stoichiometric calculation only. 7.3.4 Limitations of Concept of Oxidation Number As you have observed in the above discussion, the concept of redox processes has been evolving with time. This process of evolution is continuing. In fact, in recent past the oxidation process is visualised as a decrease in electron density and reduction process as an increase in electron density around the atom(s) involved in the reaction. 7.4 Redox Reactions and Electrode Processes The experiment corresponding to reaction (7.15), can also be observed if zinc rod is dipped in copper sulphate solution. The redox reaction takes place and during the Rationalised 2023-24 250 chemistry reaction, zinc is oxidised to zinc ions and copper ions are reduced to metallic copper due to direct transfer of electrons from zinc to copper ion. During this reaction heat is also evolved. Now we modify the experiment in such a manner that for the same redox reaction transfer of electrons takes place indirectly. This necessitates the separation of zinc metal from copper sulphate solution. We take copper sulphate solution in a beaker and put a copper strip or rod in it. We also take zinc sulphate solution in another beaker and put a zinc rod or strip in it. Now reaction takes place in either of the beakers and at the interface of the metal and its salt solution in each beaker both the reduced and oxidized forms of the same species are present. These represent the species in the reduction and oxidation half reactions. A redox couple is defined as having together the oxidised and reduced forms of a substance taking part in an oxidation or reduction half reaction. This is represented by separating the oxidised form from the reduced form by a vertical line or a slash representing an interface (e.g. solid/solution). For example in this experiment the two redox couples are represented as $Zn^{2+}/Zn$ and $Cu^{2+}/Cu$. In both cases, oxidised form is put before the reduced form. Now we put the beaker containing copper sulphate solution and the beaker containing zinc sulphate solution side by side (Fig. 7.3). We connect solutions in two beakers by a salt bridge (a U-tube containing a solution of potassium chloride or ammonium nitrate usually solidified by boiling with agar agar and later cooling to a jelly like substance). This provides an electric contact between the two solutions without allowing them to mix with each other. The zinc and copper rods are connected by a metallic wire with a provision for an ammeter and a switch. The set-up as shown in Fig.7.3 is known as Daniell cell. When the switch is in the off position, no reaction takes place in either of the beakers and no current flows through the metallic wire. As soon as the switch is in the on position, we make the following observations: 1. The transfer of electrons now does not take place directly from Zn to $Cu^{2+}$ but through the metallic wire connecting the two rods as is apparent from the arrow which indicates the flow of current. 2. The electricity from solution in one beaker to solution in the other beaker flows by the migration of ions through the salt bridge. We know that the flow of current is possible only if there is a potential difference between the copper and zinc rods known as electrodes here. The potential associated with each electrode is known as electrode potential. If the concentration of each species taking part in the electrode reaction is unity (if any gas appears in the electrode reaction, it is confined to 1 atmospheric pressure) and further the reaction is carried out at 298K, then the potential of each electrode is said to be the Standard Electrode Potential. By convention, the standard electrode potential ($E^0$) of hydrogen electrode is 0.00 volts. The electrode potential value for each electrode process is a measure of the relative tendency of the active species in the process to remain in the oxidised/reduced form. A negative $E^0$ means that the redox couple is a stronger Fig.7.3 The set-up for Daniell cell. Electrons produced at the anode due to oxidation of Zn travel through the external circuit to the cathode where these

reduce the copper ions. The circuit is completed inside the cell by the migration of ions through the salt bridge. It may be noted that the direction of current is opposite to the direction of electron flow.

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| Reaction (Oxidised form + ne$^-$ → Reduced form) | $E^0$ / V |
|---|---|
| $F_2(g) + 2e^- \rightarrow 2F^-$ | 2.87 |
| $Co^{3+} + e^- \rightarrow Co^{2+}$ | 1.81 |
| $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ | 1.78 |
| $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ | 1.51 |
| $Au^{3+} + 3e^- \rightarrow Au(s)$ | 1.40 |
| $Cl_2(g) + 2e^- \rightarrow 2Cl^-$ | 1.36 |
| $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ | 1.33 |
| $O_2(g) + 4H^+ + 4e^- \rightarrow 2H_2O$ | 1.23 |
| $MnO_2(s) + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$ | 1.23 |
| $Br_2 + 2e^- \rightarrow 2Br^-$ | 1.09 |
| $NO_3^- + 4H^+ + 3e^- \rightarrow NO(g) + 2H_2O$ | 0.97 |
| $2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$ | 0.92 |
| $Ag^+ + e^- \rightarrow Ag(s)$ | 0.80 |
| $Fe^{3+} + e^- \rightarrow Fe^{2+}$ | 0.77 |
| $O_2(g) + 2H^+ + 2e^- \rightarrow H_2O_2$ | 0.68 |
| $I_2(s) + 2e^- \rightarrow 2I^-$ | 0.54 |
| $Cu^+ + e^- \rightarrow Cu(s)$ | 0.52 |
| $Cu^{2+} + 2e^- \rightarrow Cu(s)$ | 0.34 |
| $AgCl(s) + e^- \rightarrow Ag(s) + Cl^-$ | 0.22 |
| $AgBr(s) + e^- \rightarrow Ag(s) + Br^-$ | 0.10 |
| $2H^+ + 2e^- \rightarrow H_2(g)$ | 0.00 |
| $Pb^{2+} + 2e^- \rightarrow Pb(s)$ | −0.13 |
| $Sn^{2+} + 2e^- \rightarrow Sn(s)$ | −0.14 |
| $Ni^{2+} + 2e^- \rightarrow Ni(s)$ | −0.25 |
| $Fe^{2+} + 2e^- \rightarrow Fe(s)$ | −0.44 |
| $Cr^{3+} + 3e^- \rightarrow Cr(s)$ | −0.74 |
| $Zn^{2+} + 2e^- \rightarrow Zn(s)$ | −0.76 |
| $2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-$ | −0.83 |
| $Al^{3+} + 3e^- \rightarrow Al(s)$ | −1.66 |
| $Mg^{2+} + 2e^- \rightarrow Mg(s)$ | −2.36 |
| $Na^+ + e^- \rightarrow Na(s)$ | −2.71 |
| $Ca^{2+} + 2e^- \rightarrow Ca(s)$ | −2.87 |
| $K^+ + e^- \rightarrow K(s)$ | −2.93 |
| $Li^+ + e^- \rightarrow Li(s)$ | −3.05 |

Increasing strength of oxidising agent Increasing strength of reducing agent

1. A negative $E^0$ means that the redox couple is a stronger reducing agent than the $H^+/H_2$ couple.
2. A positive $E^0$ means that the redox couple is a weaker reducing agent than the $H^+/H_2$ couple.

**Table 7.1 The Standard Electrode Potentials at 298 K**
Ions are present as aqueous species and $H_2O$ as liquid; gases and solids are shown by g and s respectively.

reducing agent than the $H^+/H_2$ couple. A positive $E^0$ means that the redox couple is a weaker reducing agent than the $H^+/H_2$ couple. The standard electrode potentials are very important and we can get a lot of other useful information from them. The values of standard electrode potentials for some selected electrode processes (reduction reactions) are given in Table 7.1. You will learn more about electrode reactions and cells in Class XII.

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**SUMMARY** Redox reactions form an important class of reactions in which oxidation and reduction occur simultaneously. Three tier conceptualisation viz, classical, electronic and oxidation number, which is usually available in the texts, has been presented in detail. Oxidation, reduction, oxidising agent (oxidant) and reducing agent (reductant) have been viewed according to each conceptualisation. Oxidation numbers are assigned in accordance with a consistent set of rules. Oxidation number and ion-electron method both are useful means in writing equations for the redox reactions. Redox reactions are classified into four categories: combination, decomposition displacement and disproportionation reactions. The concept of redox couple and electrode processes is introduced here. The redox reactions find wide applications in the study of electrode processes and cells.

**EXERCISES**

7.1 Assign oxidation number to the underlined elements in each of the following species: (a) NaH2PO4 (b) NaHSO4 (c) H4P2O7 (d) K2MnO4 (e) CaO2 (f) NaBH4 (g) H2S2O7 (h) KAl(SO4) 2.12 H2O

7.2 What are the oxidation number of the underlined elements in each of the following and how do you rationalise your results ? (a) KI3 (b) H2S4O6 (c) Fe3O4 (d) CH3CH2OH (e) CH3COOH

7.3 Justify that the following reactions are redox reactions: (a) CuO(s) + H2(g) → Cu(s) + H2O(g) (b) Fe2O3(s) + 3CO(g) → 2Fe(s) + 3CO2(g) (c) 4BCl3(g) + 3LiAlH4(s) → 2B2H6(g) + 3LiCl(s) + 3 AlCl3 (s) (d) 2K(s) + F2(g) → 2K+F− (s) (e) 4 NH3(g) + 5 O2(g) → 4NO(g) + 6H2O(g)

7.4 Fluorine reacts with ice and results in the change: H2O(s) + F2(g) → HF(g) + HOF(g) Justify that this reaction is a redox reaction.

7.5 Calculate the oxidation number of sulphur, chromium and nitrogen in H2SO5, Cr2O7 2− and NO3 − . Suggest structure of these compounds. Count for the fallacy.

7.6 Write formulas for the following compounds: (a) Mercury(II) chloride (b) Nickel(II) sulphate (c) Tin(IV) oxide (d) Thallium(I) sulphate (e) Iron(III) sulphate (f) Chromium(III) oxide

7.7 Suggest a list of the substances where carbon can exhibit oxidation states from −4 to +4 and nitrogen from −3 to +5.

7.8 While sulphur dioxide and hydrogen peroxide can act as oxidising as well as reducing agents in their reactions, ozone and nitric acid act only as oxidants. Why ?

7.9 Consider the reactions: (a) 6 CO2(g) + 6H2O(l) → C6 H12 O6(aq) + 6O2(g)

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(b) O3(g) + H2O2(l) → H2O(l) + 2O2(g) Why it is more appropriate to write these reactions as : (a)

6CO2(g) + 12H2O(l) → C6 H12 O6(aq) + 6H2O(l) + 6O2(g) (b) O3(g) + H2O2 (l) → H2O(l) + O2(g) + O2(g) Also suggest a technique to investigate the path of the above (a) and (b) redox reactions. 7.10 The compound AgF2 is unstable compound. However, if formed, the compound acts as a very strong oxidising agent. Why ? 7.11 Whenever a reaction between an oxidising agent and a reducing agent is carried out, a compound of lower oxidation state is formed if the reducing agent is in excess and a compound of higher oxidation state is formed if the oxidising agent is in excess. Justify this statement giving three illustrations. 7.12 How do you count for the following observations ? (a) Though alkaline potassium permanganate and acidic potassium permanganate both are used as oxidants, yet in the manufacture of benzoic acid from toluene we use alcoholic potassium permanganate as an oxidant. Why ? Write a balanced redox equation for the reaction. (b) When concentrated sulphuric acid is added to an inorganic mixture containing chloride, we get colourless pungent smelling gas HCl, but if the mixture contains bromide then we get red vapour of bromine. Why ? 7.13 Identify the substance oxidised reduced, oxidising agent and reducing agent for each of the following reactions: (a) 2AgBr (s) + C6H6O2(aq) → 2Ag(s) + 2HBr (aq) + C6H4O2(aq) (b) HCHO(l) + 2[Ag (NH3) 2] +(aq) + 3OH− (aq) → 2Ag(s) + HCOO− (aq) + 4NH3(aq) + 2H2O(l) (c) HCHO (l) + 2 Cu2+(aq) + 5 OH− (aq) → Cu2O(s) + HCOO− (aq) + 3H2O(l) (d) N2H4(l) + 2H2O2(l) → N2(g) + 4H2O(l) (e) Pb(s) + PbO2(s) + 2H2SO4(aq) → 2PbSO4(s) + 2H2O(l) 7.14 Consider the reactions : 2 S2O3 2− (aq) + I2(s) → S4 O6 2−(aq) + 2I− (aq) S2O3 2−(aq) + 2Br2(l) + 5 H2O(l) → 2SO4 2−(aq) + 4Br− (aq) + 10H+(aq) Why does the same reductant, thiosulphate react differently with iodine and bromine ? 7.15 Justify giving reactions that among halogens, fluorine is the best oxidant and among hydrohalic compounds, hydroiodic acid is the best reductant. 7.16 Why does the following reaction occur ? XeO6 4− (aq) + 2F− (aq) + 6H+(aq) → XeO3(g)+ F2(g) + 3H2O(l) What conclusion about the compound Na4XeO6 (of which XeO6 4− is a part) can be drawn from the reaction. 7.17 Consider the reactions: (a) H3PO2(aq) + 4 AgNO3(aq) + 2 H2O(l) → H3PO4(aq) + 4Ag(s) + 4HNO3(aq) (b) H3PO2(aq) + 2CuSO4(aq) + 2 H2O(l) → H3PO4(aq) + 2Cu(s) + H2SO4(aq) (c) C6H5CHO(l) + 2[Ag (NH3) 2] +(aq) + 3OH− (aq) → C6H5COO− (aq) + 2Ag(s) + 4NH3 (aq) + 2 H2O(l) (d) C6H5CHO(l) + 2Cu2+(aq) + 5OH− (aq) → No change observed. Rationalised 2023-24 254 chemistry What inference do you draw about the behaviour of Ag+ and Cu2+ from these reactions ? 7.18 Balance the following redox reactions by ion – electron method : (a) MnO4 – (aq) + I– (aq) → MnO2 (s) + I2(s) (in basic medium) (b) MnO4 – (aq) + SO2 (g) → Mn2+ (aq) + HSO4 – (aq) (in acidic solution) (c) H2O2 (aq) + Fe2+ (aq) → Fe3+ (aq) + H2O (l) (in acidic solution) (d) Cr2O7 2– + SO2(g) → Cr3+ (aq) + SO4 2– (aq) (in acidic solution) 7.19 Balance the following equations in basic medium by ion-electron method and oxidation number methods and identify the oxidising agent and the reducing agent. (a) P4(s) + OH– (aq) → PH3(g) + HPO2 – (aq) (b) N2H4(l) + ClO3 – (aq) → NO(g) + Cl– (g) (c) Cl2O7 (g) + H2O2(aq) → ClO2 – (aq) + O2(g) + H+ 7.20 What sorts of informations can you draw from the following reaction ? (CN)2(g) + 2OH– (aq) → CN– (aq) + CNO– (aq) + H2O(l) 7.21 The Mn3+ ion is unstable in solution and undergoes disproportionation to give Mn2+, MnO2, and H+ ion. Write a balanced ionic equation for the reaction. 7.22 Consider the elements : Cs, Ne, I and F (a) Identify the element that exhibits only negative oxidation state. (b) Identify the element that exhibits only postive oxidation state. (c) Identify the element that exhibits both positive and negative oxidation states. (d) Identify the element which exhibits neither the negative nor does the positive oxidation state. 7.23 Chlorine is used to purify drinking water. Excess of chlorine is harmful. The excess of chlorine is removed by treating with sulphur dioxide. Present a balanced equation for this redox change taking place in water. 7.24 Refer to the periodic table given in your book and now answer the following questions: (a) Select the possible non metals that can show disproportionation reaction. (b) Select three metals that can show disproportionation reaction. 7.25 In Ostwald's process for the manufacture of nitric acid, the first step involves the oxidation of ammonia gas by oxygen gas to give nitric oxide gas and steam. What is the maximum weight of nitric oxide that can be obtained starting only with 10.00 g. of ammonia and 20.00 g of oxygen ? 7.26 Using

the standard electrode potentials given in the Table 8.1, predict if the reaction between the following is feasible: (a) $Fe^{3+}$(aq) and $I^-$ (aq) (b) $Ag^+$(aq) and Cu(s) (c) $Fe^{3+}$ (aq) and Cu(s) (d) Ag(s) and $Fe^{3+}$(aq) (e) $Br_2$(aq) and $Fe^{2+}$(aq). Rationalised 2023-24 redox reactions 255 7.27 Predict the products of electrolysis in each of the following: (i) An aqueous solution of $AgNO_3$ with silver electrodes (ii) An aqueous solution $AgNO_3$ with platinum electrodes (iii) A dilute solution of $H_2SO_4$ with platinum electrodes (iv) An aqueous solution of $CuCl_2$ with platinum electrodes. 7.28 Arrange the following metals in the order in which they displace each other from the solution of their salts. Al, Cu, Fe, Mg and Zn. 7.29 Given the standard electrode potentials, $K^+/K = -2.93V$, $Ag^+/Ag = 0.80V$, $Hg^{2+}/Hg = 0.79V$ $Mg^{2+}/Mg = -2.37V$. $Cr^{3+}/Cr = -0.74V$ arrange these metals in their increasing order of reducing power. 7.30 Depict the galvanic cell in which the reaction $Zn(s) + 2Ag^+(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s)$ takes place, Further show: (i) which of the electrode is negatively charged, (ii) the carriers of the current in the cell, and (iii) individual reaction at each electrode. Rationalised 2023-24256 chemistry Organic Chemistry – Some Basic Principles and Techniques After studying this unit, you will be able to • unders tand r easons for tetravalence of carbon and shapes of organic molecules; • write structures of organic molecules in various ways; • classify the organic compounds; • name the compounds according to IUPAC system of nomenclature and also derive their structures from the given names; • understand the concept of organic reaction mechanism; • explain the influence of electronic displacements on structure and reactivity of organic compounds; • recognise the types of organic reactions; • lear n the techniques of p u r i f i c a t i o n o f o r g a n i c compounds; • write the chemical reactions involved in the qualitative analysis of organic compounds; • understand the principles involved in quantitative analysis of organic compounds. In the previous unit you have learnt that the element carbon has the unique property called catenation due to which it forms covalent bonds with other carbon atoms. It also forms covalent bonds with atoms of other elements like hydrogen, oxygen, nitrogen, sulphur, phosphorus and halogens. The resulting compounds are studied under a separate branch of chemistry called organic chemistry. This unit incorporates some basic principles and techniques of analysis required for understanding the formation and properties of organic compounds. 8.1 General Introduction Organic compounds are vital for sustaining life on earth and include complex molecules like genetic information bearing deoxyribonucleic acid (DNA) and proteins that constitute essential compounds of our blood, muscles and skin. Organic compounds appear in materials like clothing, fuels, polymers, dyes and medicines. These are some of the important areas of application of these compounds. Science of organic chemistry is about two hundred years old. Around the year 1780, chemists began to distinguish between organic compounds obtained from plants and animals and inorganic compounds prepared from mineral sources. Berzilius, a Swedish chemist proposed that a 'vital force' was responsible for the formation of organic compounds. However, this notion was rejected in 1828 when F. Wohler synthesised an organic compound, urea from an inorganic compound, ammonium cyanate. $NH_4CNO$ $NH_2CONH_2$ Ammonium cyanate Urea The pioneering synthesis of acetic acid by Kolbe (1845) and that of methane by Berthelot (1856) showed conclusively that organic compounds could be synthesised from inorganic sources in a laboratory. Unit 8 Rationalised 2023-24 organic chemistry – some basic principles and techniques 257 The development of electronic theory of covalent bonding ushered organic chemistry into its modern shape. 8.2 TETRAVALENCE OF CARBON: SHAPES OF ORGANIC COMPOUNDS 8.2.1 The Shapes of Carbon Compounds The knowledge of fundamental concepts of molecular structure helps in understanding and predicting the properties of organic compounds. You have already learnt theories of valency and molecular structure in Unit 4. Also, you already know that tetravalence of carbon and the formation of covalent bonds by it are explained in terms of its electronic configuration and the hybridisation of s and p orbitals. It may be recalled that formation and the shapes of molecules like methane ($CH_4$), ethene ($C_2H_4$), ethyne ($C_2H_2$) are explained in terms of the use of $sp^3$, $sp^2$ and sp hybrid orbitals by carbon atoms in the respective molecules.

Hybridisation influences the bond length and bond enthalpy (strength) in compounds. The sp hybrid orbital contains more s character and hence it is closer to its nucleus and forms shorter and stronger bonds than the sp3 hybrid orbital. The sp2 hybrid orbital is intermediate in s character between sp and sp3 and, hence, the length and enthalpy of the bonds it forms, are also intermediate between them. The change in hybridisation affects the electronegativity of carbon. The greater the s character of the hybrid orbitals, the greater is the electronegativity. Thus, a carbon atom having an sp hybrid orbital with 50% s character is more electronegative than that possessing sp2 or sp3 hybridised orbitals. This relative electronegativity is reflected in several physical and chemical properties of the molecules concerned, about which you will learn in later units. 8.2.2 Some Characteristic Features of $\pi$ Bonds In a $\pi$ (pi) bond formation, parallel orientation of the two p orbitals on adjacent atoms is necessary for a proper sideways overlap. Thus, in H2C=CH2 molecule all the atoms must be in the same plane. The p orbitals are mutually parallel and both the p orbitals are perpendicular to the plane of the molecule. Rotation of one CH2 fragment with respect to other interferes with maximum overlap of p orbitals and, therefore, such rotation about carbon-carbon double bond (C=C) is restricted. The electron charge cloud of the $\pi$ bond is located above and below the plane of bonding atoms. This results in the electrons being easily available to the attacking reagents. In general, $\pi$ bonds provide the most reactive centres in the molecules containing multiple bonds. Problem 8.1 How many $\sigma$ and $\pi$ bonds are present in each of the following molecules? (a) HC≡CCH=CHCH3 (b) CH2=C=CHCH3 Solution (a) $\sigma$C – C: 4; $\sigma$C–H : 6; $\pi$C=C :1; $\pi$ C≡C:2 (b) $\sigma$C – C: 3; $\sigma$C–H: 6; $\pi$C=C: 2. Problem 8.2 What is the type of hybridisation of each carbon in the following compounds? (a) CH3Cl, (b) (CH3)2CO, (c) CH3CN, (d) HCONH2, (e) CH3CH=CHCN Solution (a) sp3, (b) sp3, sp2, (c) sp3, sp, (d) sp2, (e) sp3, sp2, sp2, sp Problem 8.3 Write the state of hybridisation of carbon in the following compounds and shapes of each of the molecules. (a) H2C=O, (b) CH3F, (c) HC≡N. Solution (a) sp2 hybridised carbon, trigonal planar; (b) sp3 hybridised carbon, tetrahedral; (c) sp hybridised carbon, linear. Rationalised 2023-24 258 chemistry 8.3 STRUCTURAL RepresenTATIONS OF organic COMPOUNDs 8.3.1 Complete, Condensed and Bond-line Structural Formulas Structures of organic compounds are represented in several ways. The Lewis structure or dot structure, dash structure, condensed structure and bond line structural formulas are some of the specific types. The Lewis structures, however, can be simplified by representing the two-electron covalent bond by a dash (–). Such a structural formula focuses on the electrons involved in bond formation. A single dash represents a single bond, double dash is used for double bond and a triple dash represents triple bond. Lonepairs of electrons on heteroatoms (e.g., oxygen, nitrogen, sulphur, halogens etc.) may or may not be shown. Thus, ethane (C2H6), ethene (C2H4), ethyne (C2H2) and methanol (CH3OH) can be represented by the following structural formulas. Such structural representations are called complete structural formulas. Similarly, CH3CH2CH2CH2CH2CH2CH2CH3 can be further condensed to CH3(CH2)6CH3. For further simplification, organic chemists use another way of representing the structures, in which only lines are used. In this bond-line structural representation of organic compounds, carbon and hydrogen atoms are not shown and the lines representing carbon-carbon bonds are drawn in a zig-zag fashion. The only atoms specifically written are oxygen, chlorine, nitrogen etc. The terminals denote methyl (–CH3) groups (unless indicated otherwise by a functional group), while the line junctions denote carbon atoms bonded to appropriate number of hydrogens required to satisfy the valency of the carbon atoms. Some of the examples are represented as follows: (i) 3-Methyloctane can be represented in various forms as: (a) CH3CH2CHCH2CH2CH2CH2CH3 | CH3 These structural formulas can be further abbreviated by omitting some or all of the dashes representing covalent bonds and by indicating the number of identical groups attached to an atom by a subscript. The resulting expression of the compound is called a condensed structural formula. Thus, ethane, ethene, ethyne and methanol can be written as: CH3CH3 H2C=CH2 HC≡CH CH3OH Ethane Ethene Ethyne Methanol Ethane Ethene Ethyne Methanol

(ii) Various ways of representing 2-bromo butane are: (a) CH3CHBrCH2CH3 (b) (c) (b) (c) Rationalised 2023-24 organic chemistry – some basic principles and techniques 259 In cyclic compounds, the bond-line formulas may be given as follows: Cyclopropane Cyclopentane chlorocyclohexane Problem 8.4 Expand each of the following condensed formulas into their complete structural formulas. (a) CH3CH2COCH2CH3 (b) CH3CH=CH(CH2) 3CH3 Solution (a) (b) (b) Solution Condensed formula: (a) HO(CH2) 3CH(CH3)CH(CH3) 2 (b) HOCH(CN)2 Bond-line formula: Problem 8.5 For each of the following compounds, write a condensed formula and also their bond-line formula. (a) HOCH2CH2CH2CH(CH3)CH(CH3)CH3 (b) (a) Problem 8.6 Expand each of the following bond-line formulas to show all the atoms including carbon and hydrogen (a) (b) (c) (d) Solution Rationalised 2023-24 260 chemistry Framework model Ball and stick model Space filling model Fig. 8.2 8.3.2 Three-Dimensional Representation of Organic Molecules The three-dimensional (3-D) structure of organic molecules can be represented on paper by using certain conventions. For example, by using solid ( ) and dashed ( ) wedge formula, the 3-D image of a molecule from a two-dimensional picture can be perceived. In these formulas the solid-wedge is used to indicate a bond projecting out of the plane of paper, towards the observer. The dashed-wedge is used to depict the bond projecting out of the plane of the paper and away from the observer. Wedges are shown in such a way that the broad end of the wedge is towards the observer. The bonds lying in plane of the paper are depicted by using a normal line (—). 3-D representation of methane molecule on paper has been shown in Fig. 8.1 Fig. 8.1 Wedge-and-dash representation of CH4 Molecular Models Molecular models are physical devices that are used for a better visualisation and perception of three-dimensional shapes of organic molecules. These are made of wood, plastic or metal and are commercially available. Commonly three types of molecular models are used: (1) Framework model, (2) Ball-and-stick model, and (3) Space filling model. In the framework model only the bonds connecting the atoms of a molecule and not the atoms themselves are shown. This model emphasizes the pattern of bonds of a molecule while ignoring the size of atoms. In the ball-and-stick model, both the atoms and the bonds are shown. Balls represent atoms and the stick denotes a bond. Compounds containing C=C (e.g., ethene) can best be represented by using springs in place of sticks. These models are referred to as ball-and-spring model. The space-filling model emphasises the relative size of each atom based on its van der Waals radius. Bonds are not shown in this model. It conveys the volume occupied by each atom in the molecule. In addition to these models, computer graphics can also be used for molecular modelling. Rationalised 2023-24 organic chemistry – some basic principles and techniques 261 8.4 Classification of Organic Compounds The existing large number of organic compounds and their ever-increasing numbers has made it necessary to classify them on the basis of their structures. Organic compounds are broadly classified as follows: I. Acyclic or open chain compounds These compounds are also called as aliphatic compounds and consist of straight or branched chain compounds, for example: (homocyclic). Cyclopropane Cyclohexene Cyclohexane Sometimes atoms other than carbon are also present in the ring (heterocylic). Tetrahydrofuran given below is an example of this type of compound: Tetrahydrofuran These exhibit some of the properties similar to those of aliphatic compounds. (b) Aromatic compounds Aromatic compounds are special types of compounds. You will learn about these compounds in detail in Unit 9. These include benzene and other related ring compounds (benzenoid). Like alicyclic compounds, aromatic comounds may also have hetero atom in the ring. Such compounds are called hetrocyclic aromatic compounds. Some of the examples of various types of aromatic compounds are: Benzenoid aromatic compounds Benzene Aniline Naphthalene Non-benzenoid compound Tropone Isobutane Acetaldehyde Acetic acid CH3CH3 Ethane II Cyc l ic o r c lo sed cha in o r r ing compounds (a) Alicyclic compounds Alicyclic (aliphatic cyclic) compounds contain carbon atoms joined in the form of a ring Rationalised 2023-24 262 chemistry Heterocyclic aromatic compounds Furan Thiophene Pyridine Organic compounds can also be classified on the basis of functional groups, into families or homologous series. 8.4.1 Functional

Group The functional group is an atom or a group of atoms joined to the carbon chain which is responsible for the characteristic chemical properties of the organic compounds. The examples are hydroxyl group (–OH), aldehyde group (–CHO) and carboxylic acid group (– COOH) etc. 8.4.2 Homologous Series A group or a series of organic compounds each containing a characteristic functional group forms a homologous series and the members of the series are called homologues. The members of a homologous series can be represented by general molecular formula and the successive members differ from each other in molecular formula by a –Ch2 unit. There are a number of homologous series of organic compounds. Some of these are alkanes, alkenes, alkynes, haloalkanes, alkanols, alkanals, alkanones, alkanoic acids, amines etc. It is also possible that a compound contains two or more identical or different functional groups. This gives rise to polyfunctional compounds. 8.5 NOMENCLATURE OF ORGANIC COMPOUNDS Organic chemistry deals with millions of compounds. In order to clearly identify them, a systematic method of naming has been developed and is known as the IUPAC (International Union of Pure and Applied Chemistry) system of nomenclature. In this systematic nomenclature, the names are correlated with the structure such that the reader or listener can deduce the structure from the name. Before the IUPAC system of nomenclature, however, organic compounds were assigned names based on their origin or certain properties. For instance, citric acid is named so because it is found in citrus fruits and the acid found in red ant is named formic acid since the Latin word for ant is formica. These names are traditional and are considered as trivial or common names. Some common names are followed even today. For example, Buckminsterfullerene is a common name given to the newly discovered C60 cluster (a form of carbon) noting its structural similarity to the geodesic domes popularised by the famous architect R. Buckminster Fuller. Common names are useful and in many cases indispensable, particularly when the alternative systematic names are lengthy and complicated. Common names of some organic compounds are given in Table 8.1. Table 8.1 Common or Trivial Names of Some Organic Compounds 8.5.1 The IUPAC System of Nomenclature A systematic name of an organic compound is generally derived by identifying the parent hydrocarbon and the functional group(s) attached to it. See the example given below. Rationalised 2023-24 organic chemistry – some basic principles and techniques 263 By further using prefixes and suffixes, the parent name can be modified to obtain the actual name. Compounds containing carbon and hydrogen only are called hydrocarbons. A hydrocarbon is termed saturated if it contains only carbon-carbon single bonds. The IUPAC name for a homologous series of such compounds is alkane. Paraffin (Latin: little affinity) was the earlier name given to these compounds. Unsaturated hydrocarbons are those, which contain at least one carboncarbon double or triple bond. 8.5.2 IUPAC Nomenclature of Alkanes Straight chain hydrocarbons: The names of such compounds are based on their chain structure, and end with suffix '-ane' and carry a prefix indicating the number of carbon atoms present in the chain (except from CH4 to C4H10, where the prefixes are derived from trivial names). The IUPAC names of some straight chain saturated hydrocarbons are given in Table 8.2. The alkanes in Table 8.2 differ from each other by merely the number of -CH2 groups in the chain. They are homologues of alkane series. In order to name such compounds, the names of alkyl groups are prefixed to the name of parent alkane. An alkyl group is derived from a saturated hydrocarbon by removing a hydrogen atom from carbon. Thus, CH4 becomes -CH3 and is called methyl group. An alkyl group is named by substituting 'yl' for 'ane' in the corresponding alkane. Some alkyl groups are listed in Table 8.3. Table 8.3 Some Alkyl Groups Table 8.2 IUPAC Names of Some Unbranched Saturated Hydrocarbons Branched chain hydrocarbons: In a branched chain compound small chains of carbon atoms are attached at one or more carbon atoms of the parent chain. The small carbon chains (branches) are called alkyl groups. For example: CH3–CH–CH2–CH3 CH3–CH–CH2–CH–CH3 ▯ ▯ ▯ CH3 CH2CH3 CH3 (a) (b) Abbreviations are used for some alkyl groups. For example, methyl is abbreviated as Me, ethyl as Et, propyl as Pr and butyl as Bu. The alkyl groups can be branched also. Thus, propyl and butyl groups can have branched structures as

shown below. CH3-CH- CH3-CH2-CH- CH3-CH-CH2- ⬜ ⬜ CH3 CH3 CH3 Isopropyl- sec-Butyl- Isobutyl- ⬜ ⬜ CH3 CH3 CH3-C- CH3-C-CH2- ⬜ ⬜ CH3 CH3 tert-Butyl- NeopentylCommon branched groups have specific trivial names. For example, the propyl groups can either be n-propyl group or isopropyl group. The branched butyl groups are called sec-butyl, isobutyl and tert-butyl group. We also encounter the structural unit, –CH2C(CH3) 3, which is called neopentyl group. Nomenclature of branched chain alkanes: We encounter a number of branched chain alkanes. The rules for naming them are given below. Rationalised 2023-24 264 chemistry separated from the groups by hyphens and there is no break between methyl and nonane.] 4. If two or more identical substituent groups are present then the numbers are separated by commas. The names of identical substituents are not repeated, instead prefixes such as di (for 2), tri (for 3), tetra (for 4), penta (for 5), hexa (for 6) etc. are used. While writing the name of the substituents in alphabetical order, these prefixes, however, are not considered. Thus, the following compounds are named as: CH3 CH3 CH3 CH3 ⬜ ⬜⬜ ⬜ CH3-CH-CH2-CH-CH3 CH3⬜C ⬜CH2⬜CH ⬜CH3 1 2 3 4 5 1 2⬜ 3 4 5 2,4-Dimethylpentane 2,2,4-Trimethylpentane H3C H2C CH3 ⬜ ⬜ CH3⬜CH2⬜CH⬜C⬜CH2⬜CH2⬜CH3 1 2 3 ⬜4 5 6 7 CH3 3-Ethyl-4,4-dimethylheptane 5. If the two substituents are found in equivalent positions, the lower number is given to the one coming first in the alphabetical listing. Thus, the following compound is 3-ethyl-6-methyloctane and not 6-ethyl-3-methyloctane. 1 2 3 4 5 6 7 8 CH3 — CH2—CH—CH2—CH2—CH—CH2 —CH3 ⬜⬜ CH2CH3 CH3 6. The branched alkyl groups can be named by following the above mentioned procedures. However, the carbon atom of the branch that attaches to the root alkane is numbered 1 as exemplified below. 4 3 2 1 CH3–CH–CH2–CH– ⬜ ⬜ CH3 CH3 1,3-Dimethylbutyl1. First of all, the longest carbon chain in the molecule is identified. In the example (I) given below, the longest chain has nine carbons and it is considered as the parent or root chain. Selection of parent chain as shown in (II) is not correct because it has only eight carbons. 2. The carbon atoms of the parent chain are numbered to identify the parent alkane and to locate the positions of the carbon atoms at which branching takes place due to the substitution of alkyl group in place of hydrogen atoms. The numbering is done in such a way that the branched carbon atoms get the lowest possible numbers. Thus, the numbering in the above example should be from left to right (branching at carbon atoms 2 and 6) and not from right to left (giving numbers 4 and 8 to the carbon atoms at which branches are attached). 1 2 3 4 5 6 7 8 9 C ⬜ C ⬜ C ⬜ C ⬜ C ⬜ C ⬜ C ⬜ C ⬜⬜ C C⬜C 9 8 7 6 5 4 3 2 1 C ⬜ C ⬜ C ⬜ C ⬜ C ⬜ C ⬜ C ⬜ C ⬜ C ⬜⬜ C C ⬜ C 3. The names of alkyl groups attached as a branch are then prefixed to the name of the parent alkane and position of the substituents is indicated by the appropriate numbers. If different alkyl groups are present, they are listed in alphabetical order. Thus, name for the compound shown above is: 6-ethyl-2- methylnonane. [Note: the numbers are Rationalised 2023-24 organic chemistry – some basic principles and techniques 265 The name of such branched chain alkyl group is placed in parenthesis while naming the compound. While writing the trivial names of substituents' in alphabetical order, the prefixes iso- and neo- are considered to be the part of the fundamental name of alkyl group. The prefixes sec- and tert- are not considered to be the part of the fundamental name. The use of iso and related common prefixes for naming alkyl groups is also allowed by the IUPAC nomenclature as long as these are not further substituted. In multisubstituted compounds, the following rules may aso be remembered: • If there happens to be two chains of equal size, then that chain is to be selected which contains more number of side chains. • After selection of the chain, numbering is to be done from the end closer to the substituent. 5-(2,2-Dimethylpropyl)nonane Problem 8.7 Structures and IUPAC names of some hydrocarbons are given below. Explain why the names given in the parentheses are incorrect. 3-Ethyl-1,1-dimethylcyclohexane (not 1-ethyl-3,3-dimethylcyclohexane) Cyclic Compounds: A saturated monocyclic compound is named by prefixing 'cyclo' to the corresponding straight chain alkane. If side chains are present, then the rules given above are applied. Names of some cyclic compounds are given below. 5-sec-Butyl-4-isopropyldecane Solution (a) Lowest locant number, 2,5,6 is lower than

3,5,7, (b) substituents are in equivalent position; lower number is given to the one that comes first in the name according to alphabetical order. 2,5,6- Trimethyloctane [and not 3,4,7-Trimethyloctane] 3-Ethyl-5-methylheptane [and not 5-Ethyl-3-methylheptane] 8.5.3 N o m e n c l a t u r e o f O r g a n i c Compounds having Functional Group(s) A functional group, as defined earlier, is an atom or a group of atoms bonded together in a unique manner which is usually the site of 5-(2-Ethylbutyl)-3,3-dimethyldecane [and not 5-(2,2-Dimethylbutyl)-3-ethyldecane] Rationalised 2023-24 266 chemistry chemical reactivity in an organic molecule. Compounds having the same functional group undergo similar reactions. For example, CH3OH, CH3CH2OH, and (CH3)2CHOH — all having -OH functional group liberate hydrogen on reaction with sodium metal. The presence of functional groups enables systematisation of organic compounds into different classes. Examples of some functional groups with their prefixes and suffixes along with some examples of organic compounds possessing these are given in Table 8.4. First of all, the functional group present in the molecule is identified which determines the choice of appropriate suffix. The longest chain of carbon atoms containing the functional group is numbered in such a way that the functional group is attached at the carbon atom possessing lowest possible number in the chain. By using the suffix as given in Table 8.4, the name of the compound is arrived at. In the case of polyfunctional compounds, one of the functional groups is chosen as the principal functional group and the compound is then named on that basis. The remaining functional groups, which are subordinate functional groups, are named as substituents using the appropriate prefixes. The choice of principal functional group is made on the basis of order of preference. The order of decreasing priority for some functional groups is: -COOH, –SO3H, -COOR (R=alkyl group), COCl, -CONH2, -CN,-HC=O, >C=O, -OH, -NH2, > C=CC=O), hence suffix '-one'. Presence of two keto groups is indicated by 'di', hence suffix becomes 'dione'. The two keto groups are at carbons 2 and 4. The longest chain contains 6 carbon atoms, hence, parent hydrocarbon is hexane. Thus, the systematic name is Hexane-2,4-dione. Rationalised 2023-24 organic chemistry – some basic principles and techniques 267 Table 8.4 Some Functional Groups and Classes of Organic Compounds Rationalised 2023-24 268 chemistry Solution Here, two functional groups namely ketone and carboxylic acid are present. The principal functional group is the carboxylic acid group; hence the parent chain will be suffixed with 'oic' acid. Numbering of the chain starts from carbon of – COOH functional group. The keto group in the chain at carbon 5 is indicated by 'oxo'. The longest chain including the principal functional group has 6 carbon atoms; hence the parent hydrocarbon is hexane. The compound is, therefore, named as 5-Oxohexanoic acid. Solution The two C=C functional groups are present at carbon atoms 1 and 3, while the C≡C functional group is present at carbon 5. These groups are indicated by suffixes 'diene' and 'yne' respectively. The longest chain containing the functional groups has 6 carbon atoms; hence the parent hydrocarbon is hexane. The name of compound, therefore, is Hexa-1,3- dien-5-yne. Problem 8.9 Derive the structure of (i) 2-Chlorohexane, (ii) Pent-4-en-2-ol, (iii) 3- Nitrocyclohexene, (iv) Cyclohex-2-en-1-ol, (v) 6-Hydroxyheptanal. Solution (i) 'hexane' indicates the presence of 6 carbon atoms in the chain. The functional group chloro is present at carbon 2. Hence, the structure of the compound is CH3CH2CH2CH2CH(Cl)CH3. (ii) 'pent' indicates that parent hydrocarbon contains 5 carbon atoms in the chain. 'en' and 'ol' correspond to the functional groups C=C and -OH at carbon atoms 4 and 2 respectively. Thus, the structure is CH2=CHCH2CH (OH)CH3. (iii) Six membered ring containing a carbon-carbon double bond is implied by cyclohexene, which is numbered as shown in (I). The prefix 3-nitro means that a nitro group is present on C-3. Thus, complete structural formula of the compound is (II). Double bond is suffixed functional group whereas NO2 is prefixed functional group therefore double bond gets preference over –NO2 group: (iv) '1-ol' means that a -OH group is present at C-1. OH is suffixed functional group and gets preference over C=C bond. Thus the structure is as shown in (II): (v) 'heptanal' indicates the compound to be an aldehyde containing 7 carbon atoms in the parent chain. The '6-hydroxy' indicates that -OH group is present at carbon 6. Thus, the

structural formula of the compound is: CH3CH(OH) CH2CH2CH2CH2CHO. Carbon atom of – CHO group is included while numbering the carbon chain. 8.5.4 Nomenclature of Substituted Benzene Compounds For IUPAC nomenclature of substituted benzene compounds, the substituent is placed as prefix to the word benzene as shown in the following examples. However, common names (written in bracket below) of many substituted benzene compounds are also universally used. Rationalised 2023-24 organic chemistry – some basic principles and techniques 269 If benzene ring is disubstituted, the position of substituents is defined by numbering the carbon atoms of the ring such that the substituents are located at the lowest numbers possible. For example, the compound(b) is named as 1,3-dibromobenzene and not as 1,5-dibromobenzene. Substituent of the base compound is assigned number1 and then the direction of numbering is chosen such that the next substituent gets the lowest number. The substituents appear in the name in alphabetical order. Some examples are given below. Methylbenzene Methoxybenzene Aminobenzene (Toluene) (Anisole) (Aniline) Nitrobenzene Bromobenzene 1,2-Dibromobenzene 1,3-Dibromobenzene 1,4-Dibromobenzene (a) (b) (c) In the trivial system of nomenclature the terms ortho (o), meta (m) and para (p) are used as prefixes to indicate the relative positions 1,2;1,3 and 1,4 respectively. Thus, 1,3-dibromobenzene (b) is named as m-dibromobenzene (meta is abbreviated as m-) and the other isomers of dibromobenzene 1,2-(a) and 1,4-(c), are named as ortho (or just o-) and para (or just p-)- dibromobenzene, respectively. For tri - or higher substituted benzene derivatives, these prefixes cannot be used and the compounds are named by identifying substituent positions on the ring by following the lowest locant rule. In some cases, common name of benzene derivatives is taken as the base compound. 1-Chloro-2,4-dinitrobenzene (not 4-chloro,1,3-dinitrobenzene) 2-Chloro-1-methyl-4- nitrobenzene (not 4-methyl-5-chloro-nitrobenzene) 2-Chloro-4-methylanisole 4-Ethyl-2- methylaniline 3,4-Dimethylphenol When a benzene ring is attached to an alkane with a functional group, it is considered as substituent, instead of a parent. The name for benzene as substituent is phenyl ($C_6H_5$-, also abbreviated as Ph). Rationalised 2023-24 270 chemistry different carbon skeletons, these are referred to as chain isomers and the phenomenon is termed as chain isomerism. For example, $C_5H_{12}$ represents three compounds: Isomerism Structural isomerism Stereoisomerism Chain isomerism Position isomerism Functional group isomerism Metamerism Geometrical isomerism Optical isomerism 8.6 ISOMERISM The phenomenon of existence of two or more compounds possessing the same molecular formula but different properties is known as isomerism. Such compounds are called as isomers. The following flow chart shows different types of isomerism. 8.6.1 Structural Isomerism Compounds having the same molecular formula but different structures (manners in which atoms are linked) are classified as structural isomers. Some typical examples of different types of structural isomerism are given below: (i) Chain isomerism: When two or more compounds have similar molecular formula but (a) (b) (c) (d) Problem 8.10 Write the structural formula of: (a) o-Ethylanisole, (b) p-Nitroaniline, (c) 2,3-Dibromo-1-phenylpentane, (d) 4-Ethyl-1- fluoro-2-nitrobenzene. Solution CH3 ⬚ CH3⬚ C⬚ CH3 ⬚ CH3 Neopentane (2,2-Dimethylpropane) (ii) Position isomerism: When two or more compounds differ in the position of substituent atom or functional group on the carbon skeleton, they are called position isomers and this phenomenon is termed as position isomerism. For example, the molecular formula $C_3H_8O$ represents two alcohols: (iii) Functional group isomerism: Two or more compounds having the same molecular formula but different functional groups are called functional isomers and this phenomenon is termed as functional group isomerism. For example, the molecular formula $C_3H_6O$ represents an aldehyde and a ketone: CH3 ⬚ CH3CH2CH2CH2CH3 CH3−CHCH2CH3 Pentane Isopentane (2-Methylbutane) OH ⬚ CH3CH2CH2OH CH3−CH-CH3 Propan-1-ol Propan-2-ol Rationalised 2023-24 organic chemistry – some basic principles and techniques 271 (iv) Metamerism: It arises due to different alkyl chains on either side of the functional group in the molecule. For example, $C_4H_{10}O$ represents methoxypropane ($CH_3OC_3H_7$) and ethoxyethane ($C_2H_5OC_2H_5$). 8.6.2 Stereoisomerism The

compounds that have the same constitution and sequence of covalent bonds but differ in relative positions of their atoms or groups in space are called stereoisomers. This special type of isomerism is called as stereoisomerism and can be classified as geometrical and optical isomerism. 8.7 FUNDAMENTAL CONCEPTS IN ORGANIC REACTION MECHANISM In an organic reaction, the organic molecule (also referred as a substrate) reacts with an appropriate attacking reagent and leads to the formation of one or more intermediate(s) and finally product(s) The general reaction is depicted as follows : in understanding the reactivity of organic compounds and in planning strategy for their synthesis. In the following sections, we shall learn some of the principles that explain how these reactions take place. 8.7.1 Fission of a Covalent Bond A covalent bond can get cleaved either by : (i) heterolytic cleavage, or by (ii) homolytic cleavage. In heterolytic cleavage, the bond breaks in such a fashion that the shared pair of electrons remains with one of the fragments. After heterolysis, one atom has a sextet electronic structure and a positive charge and the other, a valence octet with at least one lone pair and a negative charge. Thus, heterolytic cleavage of bromomethane will give C + H3 and Br– as shown below. A species having a carbon atom possessing sextext of electrons and a positive charge is called a carbocation (earlier called carbonium ion). The H3 ion is known as a methyl cation or methyl carbonium ion. Carbocations are classified as primary, secondary or tertiary depending on whether one, two or three carbons are directly attached to the positively charged carbon. Some other examples of carbocations are: CH3C + H2 (ethyl cation, a primary carbocation), (CH3) 2C + H (isopropyl cation, a secondary carbocation), and (CH3) 3C + (tert-butyl cation, a tertiary carbocation). Carbocations are highly unstable and reactive species. Alkyl groups directly attached to the positively charged carbon stabilise the carbocations due to inductive and hyperconjugation effects, which you will be studying in the sections 8.7.5 and 8.7.9. The observed order of carbocation stability is: C+ H3 < CH3C + H2 < (CH3) 2C + H < (CH3) 3C + . These carbocations have trigonal planar shape with positively charged carbon being sp2 hybridised. Thus, the shape of C+ H3 may be considered as being derived from the overlap of three equivalent C(sp2) hybridised orbitals with 1s orbital of each of the three hydrogen Organic molecule (Substrate) [Intermediate] Product(s) Attacking Reagent Byproducts Substrate is that reactant which supplies carbon to the new bond and the other reactant is called reagent. If both the reactants supply carbon to the new bond then choice is arbitrary and in that case the molecule on which attention is focused is called substrate. In such a reaction a covalent bond between two carbon atoms or a carbon and some other atom is broken and a new bond is formed. A sequential account of each step, describing details of electron movement, energetics during bond cleavage and bond formation, and the rates of transformation of reactants into products (kinetics) is referred to as reaction mechanism. The knowledge of reaction mechanism helps O H ψ ξ CH3−C-CH3 CH3−CH2—C= O Propanone Propanal Rationalised 2023-24 272 chemistry atoms. Each bond may be represented as C(sp2)–H(1s) sigma bond. The remaining carbon orbital is perpendicular to the molecular plane and contains no electrons. [Fig. 8.3(a)]. Fig. 8.3 (a) Shape of methyl carbocation The heterolytic cleavage can also give a species in which carbon gets the shared pair of electrons. For example, when group Z attached to the carbon leaves without electron pair, the methyl anion is formed. Such a carbon species carrying a negative charge on carbon atom is called carbanion. Carbon in carbanion is generally sp3 hybridised and its structure is distorted tetrahedron as shown in Fig. 8.3(b). Fig. 8.3 (b) Shape of methyl carbanion Carbanions are also unstable and reactive species. The organic reactions which proceed through heterolytic bond cleavage are called ionic or heteropolar or just polar reactions. In homolytic cleavage, one of the electrons of the shared pair in a covalent bond goes with each of the bonded atoms. Thus, in homolytic cleavage, the movement of a single electron takes place instead of an electron pair. The single electron movement is shown by 'half-headed' (fish hook: ) curved arrow. Such cleavage results in the formation of neutral species (atom or group) which contains an unpaired electron. These species are called free radicals. Like carbocations and carbanions, free radicals are also very reactive. A homolytic cleavage can be

shown as: Alkyl free radical Alkyl radicals are classified as primary, secondary, or tertiary. Alkyl radical stability increases as we proceed from primary to tertiary: , Methyl Ethyl Isopropyl Tert-butyl free free free free radical radical radical radical Organic reactions, which proceed by homolytic fission are called free radical or homopolar or nonpolar reactions. 8.7.2 Substrate and Reagent Ions are generally not formed in the reactions of organic compounds. Molecules as such participate in the reaction. It is convenient to name one reagent as substrate and other as reagent. In general, a molecule whose carbon is involved in new bond formation is called substrate and the other one is called reagent. When carbon-carbon bond is formed, the choice of naming the reactants as substrate and reagent is arbitrary and depends on molecule under observation. Example: (i) $CH_2 = CH_2 + Br_2 \rightarrow CH_2 Br – CH_2Br$ Substrate Reagent Product (ii) Nucleophiles and Electrophiles Reagents attack the reactive site of the substrate. The reactive site may be electron Rationalised 2023-24 organic chemistry – some basic principles and techniques 273 deficient portion of the molecule (a positive reactive site) e.g., an atom with incomplete electron shell or the positive end of the dipole in the molecule. If the attacking species is electron rich, it attacks these sites. If attacking species is electron deficient, the reactive site for it is that part of the substrate molecule which can supply electrons, e.g., $\pi$ electrons in a double bond. A reagent that brings an electron pair to the reactive site is called a nucleophile (Nu:) i.e., nucleus seeking and the reaction is then called nucleophilic. A reagent that takes away an electron pair from reactive site is called electrophile (E+) i.e., electron seeking and the reaction is called electrophilic. During a polar organic reaction, a nucleophile attacks an electrophilic centre of the substrate which is that specific atom or part of the substrate which is electron deficient. Similarly, the electrophiles attack at nucleophilic centre, which is the electron rich centre of the substrate. Thus, the electrophiles receive electron pair from the substrate when the two undergo bonding interaction. A curved-arrow notation is used to show the movement of an electron pair from the nucleophile to the electrophile. Some examples of nucleophiles are the negatively charged ions with lone pair of electrons such as hydroxide (HO–), cyanide (NC–) ions and carbanions ($R_3C^{:–}$). Neutral molecules such as etc., can also act as nucleophiles due to the presence of lone pair of electrons. Examples of electrophiles include carbocations ($C^+H_3$) and neutral molecules having functional groups like carbonyl group (>C=O) or alkyl halides (R3C-X, where X is a halogen atom). The carbon atom in carbocations has sextet configuration; hence, it is electron deficient and can receive a pair of electrons from the nucleophiles. In neutral molecules such as alkyl halides, due to the polarity of the C-X bond a partial positive charge is generated on the carbon atom and hence the carbon atom becomes an electrophilic centre at which a nucleophile can attack. Problem 8.11 Using curved-arrow notation, show the formation of reactive intermediates when the following covalent bonds undergo heterolytic cleavage. (a) CH3–SCH3, (b) CH3–CN, (c) CH3–Cu Solution Problem 8.12 Giving justification, categorise the following molecules/ions as nucleophile or electrophile: Solution Nucleophiles: HS–, C2H5O–, (CH3)3N:H2N:– These species have unshared pair of electrons, which can be donated and shared with an electrophile. Electrophiles: BF3, Cl+H3–C+ =O,N+ O2. Reactive sites have only six valence electrons; can accept electron pair from a nucleophile. Problem 8.13 Identify electrophilic centre in the following: CH3CH=O, CH3CN, CH3I. Solution Among CH3HC*=O, H3CC*≡N, and H3C* –I, the starred carbon atoms are electrophilic centers as they will have partial positive charge due to polarity of the bond. 8.7.3 Electron Movement in Organic Reactions The movement of electrons in organic reactions can be shown by curved-arrow Rationalised 2023-24 274 chemistry notation. It shows how changes in bonding occur due to electronic redistribution during the reaction. To show the change in position of a pair of electrons, curved arrow starts from the point from where an electron pair is shifted and it ends at a location to which the pair of electron may move. Presentation of shifting of electron pair is given below : (i) from $\pi$ bond to adjacent bond position (ii) from $\pi$ bond to adjacent atom (iii) from atom to adjacent bond position Movement of single electron is indicated by a single barbed 'fish hooks' (i.e. half headed curved arrow). For

example, in transfer of hydroxide ion giving ethanol and in the dissociation of chloromethane, the movement of electron using curved arrows can be depicted as follows: 8.7.4 Electron Displacement Effects in Covalent Bonds The electron displacement in an organic molecule may take place either in the ground state under the influence of an atom or a substituent group or in the presence of an appropriate attacking reagent. The electron displacements due to the influence of an atom or a substituent group present in the molecule cause permanent polarlisation of the bond. Inductive effect and resonance effects are examples of this type of electron displacements. Temporary electron displacement effects are seen in a molecule when a reagent approaches to attack it. This type of electron displacement is called electromeric effect or polarisability effect. In the following sections we will learn about these types of electronic displacements. 8.7.5 Inductive Effect When a covalent bond is formed between atoms of different electronegativity, the electron density is more towards the more electronegative atom of the bond. Such a shift of electron density results in a polar covalent bond. Bond polarity leads to various electronic effects in organic compounds. Let us consider cholorethane ($CH_3CH_2Cl$) in which the C–Cl bond is a polar covalent bond. It is polarised in such a way that the carbon-1 gains some positive charge ($\delta+$) and the chlorine some negative charge ($\delta-$ ). The fractional electronic charges on the two atoms in a polar covalent bond are denoted by symbol $\delta$ (delta) and the shift of electron density is shown by an arrow that points from $\delta+$ to $\delta-$ end of the polar bond. $\delta\delta+$ $\delta+$ $\delta-$ $CH_3 \rightarrow CH_2 \rightarrow Cl$ 2 1 In turn carbon-1, which has developed partial positive charge ($\delta+$) draws some electron density towards it from the adjacent C-C bond. Consequently, some positive charge ($\delta\delta+$) develops on carbon-2 also, where $\delta\delta+$ symbolises relatively smaller positive charge as compared to that on carbon – 1. In other words, the polar C – Cl bond induces polarity in the adjacent bonds. Such polarisation of $\sigma$-bond caused by the polarisation of adjacent $\sigma$-bond is referred to as the inductive effect. This effect is passed on to the subsequent bonds also but the effect decreases rapidly as the number of intervening bonds increases and becomes vanishingly small after three bonds. The inductive effect is related to the ability of substituent(s) to either withdraw or donate electron density to the attached carbon atom. Based on this ability, the substitutents can be classified as electron-withdrawing or electron donating groups relative to hydrogen. Halogens and many other groups such as nitro (- $NO_2$), cyano (- CN), carboxy (- COOH), ester (COOR), aryloxy (-OAr, e.g. – $OC_6H_5$), etc. are electron-withdrawing groups. On the other hand, the alkyl groups like methyl (–$CH_3$) and ethyl (–$CH_2$–$CH_3$) are usually considered as electron donating groups. Rationalised 2023-24 organic chemistry – some basic principles and techniques 275 Problem 8.14 Which bond is more polar in the following pairs of molecules: (a) $H_3C$-H, $H_3C$-Br (b) $H_3C$-$NH_2$, $H_3C$-OH (c) $H_3C$-OH, $H_3C$-SH Solution (a) C–Br, since Br is more electronegative than H, (b) C–O, (c) C–O Problem 8.15 In which C–C bond of $CH_3CH_2CH_2Br$, the inductive effect is expected to be the least? Solution Magnitude of inductive effect diminishes as the number of intervening bonds increases. Hence, the effect is least in the bond between carbon-3 and hydrogen. 8.7.6 Resonance Structure There are many organic molecules whose behaviour cannot be explained by a single Lewis structure. An example is that of benzene. Its cyclic structure containing alternating C–C single and C=C double bonds shown is inadequate for explaining its characteristic properties. As per the above representation, benzene should exhibit two different bond lengths, due to C–C single and C=C double bonds. However, as determined experimentally benzene has a uniform C–C bond distances of 139 pm, a value intermediate between the C–C single(154 pm) and C=C double (134 pm) bonds. Thus, the structure of benzene cannot be represented adequately by the above structure. Further, benzene can be represented equally well by the energetically identical structures I and II. benzene cannot be adequately represented by any of these structures, rather it is a hybrid of the two structures (I and II) called resonance structures. The resonance structures (canonica l structures or contributing structures) are hypothetical and individually do not represent any real molecule. They contribute to the actual structure in proportion to their stability. Another

example of resonance is provided by nitromethane (CH3NO2) which can be represented by two Lewis structures, (I and II). There are two types of N-O bonds in these structures. However, it is known that the two N–O bonds of nitromethane are of the same length (intermediate between a N–O single bond and a N=O double bond). The actual structure of nitromethane is therefore a resonance hybrid of the two canonical forms I and II. The energy of actual structure of the molecule (the resonance hybrid) is lower than that of any of the canonical structures. The difference in energy between the actual structure and the lowest energy resonance structure is called the resonance stabilisation energy or simply the resonance energy. The more the number of important contributing structures, the more is the resonance energy. Resonance is particularly important when the contributing structures are equivalent in energy. The following rules are applied while writing resonance structures: The resonance structures have (i) the same positions of nuclei and (ii) the same number of unpaired electrons. Among the resonance structures, the one which has more number of covalent bonds, all the atoms with octet of electrons (except hydrogen which has a duplet), less separation of opposite charges, (a negative charge if any on more electronegative atom, a positive charge if any on more electropositive atom) and more dispersal of charge, is more stable than others. Benzene Therefore, according to the resonance theory (Unit 4) the actual structure of Rationalised 2023-24 276 chemistry Problem 8.16 Write resonance structures of CH3COO– and show the movement of electrons by curved arrows. Solution First, write the structure and put unshared pairs of valence electrons on appropriate atoms. Then draw the arrows one at a time moving the electrons to get the other structures. Problem 8.17 Write resonance structures of CH2=CH–CHO. Indicate relative stability of the contributing structures. Solution Solution The two structures are less important contributors as they involve charge separation. Additionally, structure I contains a carbon atom with an incomplete octet. 8.7.7 Resonance Effect The resonance effect is defined as 'the polarity produced in the molecule by the interaction of two $\pi$-bonds or between a $\pi$-bond and lone pair of electrons present on an adjacent atom'. The effect is transmitted through the chain. There are two types of resonance or mesomeric effect designated as R or M effect. (i) Positive Resonance Effect (+R effect) In this effect, the transfer of electrons is away from an atom or substituent group attached to the conjugated system. This electron displacement makes certain positions in the molecule of high electron densities. This effect in aniline is shown as : Stability: I > II > III [I: Most stable, more number of covalent bonds, each carbon and oxygen atom has an octet and no separation of opposite charge II: negative charge on more electronegative atom and positive charge on more electropositive atom; III: does not contribute as oxygen has positive charge and carbon has negative charge, hence least stable]. Problem 8.18 Explain why the following two structures, I and II cannot be the major contributors to the real structure of CH3COOCH3. (ii) Negative Resonance Effect (- R effect) This effect is observed when the transfer of electrons is towards the atom or substituent group attached to the conjugated system. For example in nitrobenzene this electron displacement can be depicted as : The atoms or substituent groups, which represent +R or –R electron displacement effects are as follows : +R effect: – halogen, –OH, –OR, –OCOR, –NH2, –NHR, –NR2, –NHCOR, – R effect: – COOH, – CHO, >C=O, – CN, –NO2 Rationalised 2023-24 organic chemistry – some basic principles and techniques 277 The presence of alternate single and double bonds in an open chain or cyclic system is termed as a conjugated system. These systems often show abnormal behaviour. The examples are 1,3- butadiene, aniline and nitrobenzene etc. In such systems, the $\pi$-electrons are delocalised and the system develops polarity. 8.7.8 Electromeric Effect (E effect) It is a temporary effect. The organic compounds having a multiple bond (a double or triple bond) show this effect in the presence of an attacking reagent only. It is defined as the complete transfer of a shared pair of $\pi$-electrons to one of the atoms joined by a multiple bond on the demand of an attacking reagent. The effect is annulled as soon as the attacking reagent is removed from the domain of the reaction. It is represented by E and the shifting of the electrons is shown by a curved arrow ( ). There are two distinct types of

electromeric effect. (i) Positive Eelctromeric Effect (+E effect) In this effect the $\pi$–electrons of the multiple bond are transferred to that atom to which the reagent gets attached. For example: system or to an atom with an unshared p orbital. The $\sigma$ electrons of C—H bond of the alkyl group enter into partial conjugation with the attached unsaturated system or with the unshared p orbital. Hyperconjugation is a permanent effect. To understand hyperconjugation effect, let us take an example of $CH_3\overset{+}{C}H_2$ (ethyl cation) in which the positively charged carbon atom has an empty p orbital. One of the C-H bonds of the methyl group can align in the plane of this empty p orbital and the electrons constituting the C-H bond in plane with this p orbital can then be delocalised into the empty p orbital as depicted in Fig. 8.4 (a). (ii) Negative Electromeric Effect (–E effect) In this effect the $\pi$ - electrons of the multiple bond are transferred to that atom to which the attacking reagent does not get attached. For example: When inductive and electromeric effects operate in opposite directions, the electomeric effect predominates. 8.7.9 Hyperconjugation Hyperconjugation is a general stabilising interaction. It involves delocalisation of $\sigma$ electrons of C—H bond of an alkyl group directly attached to an atom of unsaturated Fig. 8.4(a) Orbital diagram showing hyperconjugation in ethyl cation This type of overlap stabilises the carbocation because electron density from the adjacent $\sigma$ bond helps in dispersing the positive charge. In general, greater the number of alkyl groups attached to a positively charged carbon atom, the greater is the hyperconjugation interaction and stabilisation of the cation. Thus, we have the following relative stability of carbocations : Rationalised 2023-24 278 chemistry Hyperconjugation is also possible in alkenes and alkylarenes. D e l o c a l i s a t i o n o f e l e c t r o n s b y hyperconjugation in the case of alkene can be depicted as in Fig. 8.4(b). Problem 8.19 Explain why $(CH_3)_3\overset{+}{C}$ is more stable than $CH_3\overset{+}{C}H_2$ and $\overset{+}{C}H_3$ is the least stable cation. Solution Hyperconjugation interaction in $(CH_3)_3\overset{+}{C}$ is greater than in $CH_3\overset{+}{C}H_2$ as the $(CH_3)_3\overset{+}{C}$ has nine C-H bonds. In $\overset{+}{C}H_3$, vacant p orbital is perpendicular to the plane in which C-H bonds lie; hence cannot overlap with it. Thus, $\overset{+}{C}H_3$ lacks hyperconjugative stability. 8.7.10 Types of Organic Reactions and Mechanisms Organic reactions can be classified into the following categories: (i) Substitution reactions (ii) Addition reactions (iii) Elimination reactions (iv) Rearrangement reactions You will be studying these reactions in Unit 9 and later in class XII. 8.8 Methods of Purification of Organic Compounds Once an organic compound is extracted from a natural source or synthesised in the laboratory, it is essential to purify it. Various methods used for the purification of organic compounds are based on the nature of the compound and the impurity present in it. The common techniques used for purification are as follows : (i) Sublimation (ii) Crystallisation (iii) Distillation (iv) Differential extraction and (v) Chromatography Finally, the purity of a compound is ascertained by determining its melting or boiling point. Most of the pure compounds have sharp melting points and boiling points. New methods of checking the purity of an organic compound are based on different Fig. 8.4(b) Orbital diagram showing hyperconjugation in propene There are various ways of looking at the hyperconjugative effect. One of the way is to regard C—H bond as possessing partial ionic character due to resonance. The hyperconjugation may also be regarded as no bond resonance. Rationalised 2023-24 organic chemistry – some basic principles and techniques 279 types of chromatographic and spectroscopic techniques. 8.8.1 Sublimation You have learnt earlier that on heating, some solid substances change from solid to vapour state without passing through liquid state. The purification technique based on the above principle is known as sublimation and is used to separate sublimable compounds from nonsublimable impurities. 8.8.2 Crystallisation This is one of the most commonly used techniques for the purification of solid organic compounds. It is based on the difference in the solubilities of the compound and the impurities in a suitable solvent. The impure compound is dissolved in a solvent in which it is sparingly soluble at room temperature but appreciably soluble at higher temperature. The solution is concentrated to get a nearly saturated solution. On cooling the solution, pure compound crystallises out and is removed by filtration. The filtrate (mother liquor) contains impurities and small quantity of the compound. If the compound is

highly soluble in one solvent and very little soluble in another solvent, crystallisation can be satisfactorily carried out in a mixture of these solvents. Impurities, which impart colour to the solution are removed by adsorbing over activated charcoal. Repeated crystallisation becomes necessary for the purification of compounds containing impurities of comparable solubilities. 8.8.3 Distillation This important method is used to separate (i) volatile liquids from nonvolatile impurities and (ii) the liquids having sufficient difference in their boiling points. Liquids having different boiling points vaporise at different temperatures. The vapours are cooled and the liquids so formed are collected separately. Chloroform (b.p 334 K) and aniline (b.p. 457 K) are easily separated by the technique of distillation (Fig 8.5). The liquid mixture is taken in a round bottom flask and heated carefully. On boiling, the vapours of lower boiling component are formed first. The vapours are condensed by using a condenser and the liquid is collected in a receiver. The vapours of higher boiling component form later and the liquid can be collected separately. Fractional Distillation: If the difference in boiling points of two liquids is not much, simple distillation cannot be used to separate them. The vapours of such liquids are formed within the same temperature range and are condensed simultaneously. The technique of fractional distillation is used in such cases. In this technique, vapours of a liquid mixture are passed through a fractionating column before condensation. The fractionating column is fitted over the mouth of the round bottom flask (Fig.8.6, page 280). Vapours of the liquid with higher boiling point condense before the vapours of the liquid with lower boiling point. The vapours rising up in the fractionating column become richer in more volatile component. By the Fig.8.5 Simple distillation. The vapours of a substance formed are condensed and the liquid is collected in conical flask. Rationalised 2023-24 280 chemistry time the vapours reach to the top of the fractionating column, these are rich in the more volatile component. Fractionating columns are available in various sizes and designs as shown in Fig.8.7. A fractionating column provides many surfaces for heat exchange between the ascending vapours and the descending condensed liquid. Some of the condensing liquid in the fractionating column obtains heat from the ascending vapours and revaporises. The vapours thus become richer in low boiling component. The vapours of low boiling component ascend to the top of the column. On reaching the top, the vapours become pure in low boiling component and pass through the condenser and the pure liquid is collected in a receiver. After a series of successive distillations, the remaining liquid in the distillation flask gets enriched in high boiling component. Each successive condensation and vaporisation Fig.8.7 Different types of fractionating columns. unit in the fractionating column is called a theoretical plate. Commercially, columns with hundreds of plates are available. One of the technological applications of fractional distillation is to separate different fractions of crude oil in petroleum industry. Fig.8.6 Fractional distillation. The vapours of lower boiling fraction reach the top of the column first followed by vapours of higher boiling fractions. Distillation under reduced pressure: This method is used to purify liquids having very high boiling points and those, which decompose at or below their boiling points. Such liquids are made to boil at a temperature lower than their normal boiling points by reducing the pressure on their surface. A liquid boils at a temperature at which its vapour pressure is equal to the external pressure. The pressure is reduced with the help of a water pump or vacuum pump (Fig.8.8). Glycerol can be separated from spent-lye in soap industry by using this technique. Rationalised 2023-24 organic chemistry – some basic principles and techniques 281 Fig.8.8 Distillation under reduced pressure. A liquid boils at a temperature below its vapour pressure by reducing the pressure. Steam Distillation: This technique is applied to separate substances which are steam volatile and are immiscible with water. In steam distillation, steam from a steam generator is passed through a heated flask containing the liquid to be distilled. The mixture of steam and the volatile organic compound is condensed and collected. The compound is later separated from water using a separating funnel. In steam distillation, the liquid boils when the sum of vapour pressures due to the organic liquid ($p_1$) and that due to water ($p_2$) becomes equal to the atmospheric pressure

(p), i.e. p =p1+ p2. Since p1 is lower than p, the organic liquid vaporises at lower temperature than its boiling point. Thus, if one of the substances in the mixture is water and the other, a water insoluble substance, then the mixture will boil close to but below, 373K. A mixture of water and the substance is obtained which can be separated by using a separating funnel. Aniline is separated by this technique from aniline – water mixture (Fig.8.9, Page 282). 8.8.4 Differential Extraction When an organic compound is present in an aqueous medium, it is separated by shaking it with an organic solvent in which it is more soluble than in water. The organic solvent and the aqueous solution should be immiscible with each other so that they form two distinct layers which can be separated by separatory funnel. The organic solvent is later removed by distillation or by evaporation to get back the compound. Differential extraction is carried out in a separatory funnel as shown in Fig. 8.10 (Page 282). If the organic compound is less soluble in the organic solvent, a very large quantity of solvent would be required to extract even a very small quantity of the compound. The technique of continuous extraction is employed in such cases. In this technique same solvent is repeatedly used for extraction of the compound. 8.8.5 Chromatography Chromatography is an important technique extensively used to separate mixtures into their components, purify compounds and also to test the purity of compounds. The Rationalised 2023-24 282 chemistry name chromatography is based on the Greek word chroma, for colour since the method was first used for the separation of coloured substances found in plants. In this technique, the mixture of substances is applied onto a stationary phase, which may be a solid or a liquid. A pure solvent, a mixture of solvents, or a gas is allowed to move slowly over the stationary phase. The components of the mixture get gradually separated from one another. The moving phase is called the mobile phase. Based on the principle involved, chromatography is classified into different categories. Two of these are: (a) Adsorption chromatography, and (b) Partition chromatography. a) Adsorption Chromatography: Adsorption chromatography is based on the fact that different compounds are adsorbed on an adsorbent to different degrees. Commonly used adsorbents are silica gel and alumina. When a mobile phase is allowed to move over a stationary phase (adsorbent), the components of the mixture move by varying distances over the stationary phase. Following are two main types of chromatographic techniques based on the principle of differential adsorption. (a) Column chromatography, and (b) Thin layer chromatography. Fig.8.10 Differential extraction. Extraction of compound takes place based on difference in solubility Fig.8.9 Steam distillation. Steam volatile component volatilizes, the vapours condense in the condenser and the liquid collects in conical flask. Rationalised 2023-24 organic chemistry – some basic principles and techniques 283 Column Chromatography: Column chromatography involves separation of a mixture over a column of adsorbent (stationary phase) packed in a glass tube. The column is fitted with a stopcock at its lower end (Fig. 8.11). The mixture adsorbed on adsorbent is placed on the top of the adsorbent column packed in a glass tube. An appropriate eluant which is a liquid or a mixture of liquids is allowed to flow down the column slowly. Depending upon the degree to which the compounds are adsorbed, complete separation takes place. The most readily adsorbed substances are retained near the top and others come down to various distances in the column (Fig.8.11). The glass plate is then placed in a closed jar containing the eluant (Fig. 8.12a). As the eluant rises up the plate, the components of the mixture move up along with the eluant to different distances depending on their degree of adsorption and separation takes place. The relative adsorption of each component of the mixture is expressed in terms of its retardation factor i.e. Rf value (Fig.8.12 b). Rf = Distance moved by the substance from base line (x) Distance moved by the solvent from base line (y) Fig.8.11 Column chromatography. Different stages of separation of components of a mixture. Thin Layer Chromatography: Thin layer chromatography (TLC) is another type of adsorption chromatography, which involves separation of substances of a mixture over a thin layer of an adsorbent coated on glass plate. A thin layer (about 0.2mm thick) of an adsorbent (silica gel or alumina) is spread over a glass plate of suitable size. The plate is known as

thin layer chromatography plate or chromaplate. The solution of the mixture to be separated is applied as a small spot about 2 cm above one end of the TLC plate. The spots of coloured compounds are visible on TLC plate due to their original colour. The spots of colourless compounds, which are invisible to the eye but fluoresce in ultraviolet light, can be detected by putting the plate under ultraviolet light. Another detection technique is to place the plate in a covered jar containing a few crystals of iodine. Spots of compounds, which adsorb iodine, will show up as brown spots. Sometimes an appropriate reagent may also be sprayed on the plate. For example, amino acids may be detected by spraying the plate with ninhydrin solution (Fig.8.12b). Fig.8.12 (b) Developed chromatogram. Fig.8.12 (a) Thin layer chromatography. Chromatogram being developed. Rationalised 2023-24 284 chemistry spot on the chromatogram. The spots of the separated colourless compounds may be observed either under ultraviolet light or by the use of an appropriate spray reagent as discussed under thin layer chromatography. 8.9 Qualitative Analysis of Organic Compounds The elements present in organic compounds are carbon and hydrogen. In addition to these, they may also contain oxygen, nitrogen, sulphur, halogens and phosphorus. 8.9.1 Detection of Carbon and Hydrogen Carbon and hydrogen are detected by heating the compound with copper(II) oxide. Carbon present in the compound is oxidised to carbon dioxide (tested with lime-water, which develops turbidity) and hydrogen to water (tested with anhydrous copper sulphate, which turns blue). $C + 2CuO \rightarrow 2Cu + CO_2$ $2H + CuO \rightarrow Cu + H_2O$ $CO_2 + Ca(OH)_2 \rightarrow CaCO_3\downarrow + H_2O$ $5H_2O + CuSO_4 \rightarrow CuSO_4.5H_2O$ White Blue 8.9.2 Detection of Other Elements Nitrogen, sulphur, halogens and phosphorus present in an organic compound are detected by "Lassaigne's test". The elements present in the compound are converted from covalent form into the ionic form by fusing the compound with sodium metal. Following reactions take place: $Na + C + N \rightarrow NaCN$ $2Na + S \rightarrow Na_2S$ $Na + X \rightarrow Na X$ (X = Cl, Br or I) C, N, S and X come from organic compound. Cyanide, sulphide and halide of sodium so formed on sodium fusion are extracted from the fused mass by boiling it with distilled water. This extract is known as sodium fusion extract. (A) Test for Nitrogen The sodium fusion extract is boiled with iron(II) sulphate and then acidified with Partition Chromatography: Partition chromatography is based on continuous differential partitioning of components of a mixture between stationary and mobile phases. Paper chromatography is a type of partition chromatography. In paper chromatography, a special quality paper known as chromatography paper is used. Chromatography paper contains water trapped in it, which acts as the stationary phase. A strip of chromatography paper spotted at the base with the solution of the mixture is suspended in a suitable solvent or a mixture of solvents (Fig. 8.13). This solvent acts as the mobile phase. The solvent rises up the paper by capillary action and flows over the spot. The paper selectively retains different components according to their differing partition in the two phases. The paper strip so developed is known as a chromatogram. The spots of the separated coloured compounds are visible at different heights from the position of initial Fig.8.13 Paper chromatography. Chromatography paper in two different shapes. Rationalised 2023-24 organic chemistry – some basic principles and techniques 285 concentrated sulphuric acid. The formation of Prussian blue colour confirms the presence of nitrogen. Sodium cyanide first reacts with iron(II) sulphate and forms sodium hexacyanidoferrate(II). On heating with concentrated sulphuric acid some iron(II) ions are oxidised to iron(III) ions which react with sodium hexacyanidoferrate(II) to produce iron(III) hexacyanidoferrate(II) (ferriferrocyanide) which is Prussian blue in colour. $6CN^- + Fe^{2+} \rightarrow [Fe(CN)_6]^{4-}$ $3[Fe(CN)_6]^{4-} + 4Fe^{3+} \rightarrow Fe_4[Fe(CN)_6]_3.xH_2O$ Prussian blue (B) Test for Sulphur (a) The sodium fusion extract is acidified with acetic acid and lead acetate is added to it. A black precipitate of lead sulphide indicates the presence of sulphur. $S^{2-} + Pb^{2+} \rightarrow PbS$ Black (b) On treating sodium fusion extract with sodium nitroprusside, appearance of a violet colour further indicates the presence of sulphur. $S^{2-} + [Fe(CN)_5NO]^{2-} \rightarrow [Fe(CN)_5NOS]^{4-}$ Violet In case, nitrogen and sulphur both are present in an organic compound, sodium thiocyanate is formed. It gives blood red colour and no

Prussian blue since there are no free cyanide ions. Na + C + N + S $\rightarrow$ NaSCN Fe3+ +SCN− $\rightarrow$ [Fe(SCN)]2+ Blood red If sodium fusion is carried out with excess of sodium, the thiocyanate decomposes to yield cyanide and sulphide. These ions give their usual tests. NaSCN + 2Na $\rightarrow$ NaCN+Na2S (C) Test for Halogens The sodium fusion extract is acidified with nitric acid and then treated with silver nitrate. A white precipitate, soluble in ammonium hydroxide shows the presence of chlorine, a yellowish precipitate, sparingly soluble in ammonium hydroxide shows the presence of bromine and a yellow precipitate, insoluble in ammonium hydroxide shows the presence of iodine. X− + Ag+ $\rightarrow$ AgX X represents a halogen – Cl, Br or I. If nitrogen or sulphur is also present in the compound, the sodium fusion extract is first boiled with concentrated nitric acid to decompose cyanide or sulphide of sodium formed during Lassaigne's test. These ions would otherwise interfere with silver nitrate test for halogens. (D) Test for Phosphorus The compound is heated with an oxidising agent (sodium peroxide). The phosphorus present in the compound is oxidised to phosphate. The solution is boiled with nitric acid and then treated with ammonium molybdate. A yellow colouration or precipitate indicates the presence of phosphorus. Na3PO4 + 3HNO3 $\rightarrow$ H3PO4+3NaNO3 H3PO4 + 12(NH4) 2MoO4 + 21HNO3 $\rightarrow$ Ammonium molybdate (NH4) 3PO4.12MoO3 + 21NH4NO3 + 12H2O Ammonium phosphomolybdate 8.10 Quantitative Analysis Quantitative analysis of compounds is very important in organic chemistry. It helps chemists in the determination of mass per cent of elements present in a compound. You have learnt in Unit-1 that mass per cent of elements is required for the determination of emperical and molecular formula. The percentage composition of elements present in an organic compound is determined by the following methods: 8.10.1 Carbon and Hydrogen Both carbon and hydrogen are estimated in one experiment. A known mass of an organic compound is burnt in the presence of excess of oxygen and copper(II) oxide. Carbon and hydrogen in the compound are oxidised to carbon dioxide and water respectively. Cx Hy + (x + y/4) O2 $\rightarrow$ x CO2 + (y/2) H2O Rationalised 2023-24 286 chemistry The mass of water produced is determined by passing the mixture through a weighed U-tube containing anhydrous calcium chloride. Carbon dioxide is absorbed in another U-tube containing concentrated solution of potassium hydroxide. These tubes are connected in series (Fig. 8.14). The increase in masses of calcium chloride and potassium hydroxide gives the amounts of water and carbon dioxide from which the percentages of carbon and hydrogen are calculated. Let the mass of organic compound be m g, mass of water and carbon dioxide produced be m1 and m2 g respectively; Percentage of carbon= 2 12 100 44 m m × × × Percentage of hydrogen = 1 2 100 18 m m × × × Problem 8.20 On complete combustion, 0.246 g of an organic compound gave 0.198g of carbon dioxide and 0.1014g of water. Determine the percentage composition of carbon and hydrogen in the compound. Solution 12 0.198 100 Percentage of carbon 44 0.246 21.95% × × = × = Percentage of hydrogen 2 0.1014 100 18 0.246 4.58% × × = × = 8.10.2 Nitrogen There are two methods for estimation of nitrogen: (i) Dumas method and (ii) Kjeldahl's method. (i) Dumas method: The nitrogen containing organic compound, when heated with copper oxide in an atmosphere of carbon dioxide, yields free nitrogen in addition to carbon dioxide and water. Cx Hy Nz + (2x + y/2) CuO $\rightarrow$ x CO2 + y/2 H2O + z/2 N2 + (2x + y/2) Cu Traces of nitrogen oxides formed, if any, are reduced to nitrogen by passing the gaseous mixture over a heated copper gauze. The mixture of gases so produced is collected over an aqueous solution of potassium hydroxide which absorbs carbon dioxide. Nitrogen is collected in the upper part of the graduated tube (Fig.8.15). Let the mass of organic compound = m g Volume of nitrogen collected = V1 mL Room temperature = T1K 1 1 1 273 Volume of nitrogen at STP 760 (Let it be mL) PV T V × = × Where p1 and V1 are the pressure and volume of nitrogen, p1 is different from the atmospheric pressure at which nitrogen gas is collected. The value of p1 is obtained by the relation; p1= Atmospheric pressure – Aqueous tension 22400 mL N2 at STP weighs 28 g. Fig.8.14 Estimation of carbon and hydrogen. Water and carbon dioxide formed on oxidation of substance are absorbed in anhydrous calcium chloride and potassium hydroxide solutions respectively contained in U tubes.

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2 28 mL N at STP weighs g 22400 V V × = Percentage of nitrogen = 28 100 22400 V m × × × Problem 8.21 In Dumas' method for estimation of nitrogen, 0.3g of an organic compound gave 50mL of nitrogen collected at 300K temperature and 715mm pressure. Calculate the percentage composition of nitrogen in the compound. (Aqueous tension at 300K=15 mm) Solution Volume of nitrogen collected at 300K and 715mm pressure is 50 mL Actual pressure = 715-15 =700 mm 273 700 50 Volume of nitrogen at STP 300 760 41.9mL × × × 22,400 mL of N2 at STP weighs = 28 g 28 41.9 41.9mL of nitrogen weighs 22400 g × = 28 41.9 100 Percentage of nitrogen 22400 0.3 17.46% × × = × = Fig. 8.15 Dumas method. The organic compound yields nitrogen gas on heating it with copper(II) oxide in the presence of CO2 gas. The mixture of gases is collected over potassium hydroxide solution in which CO2 is absorbed and volume of nitrogen gas is determined. (ii) Kjeldahl's method: The compound containing nitrogen is heated with concentrated sulphuric acid. Nitrogen in the compound gets converted to ammonium sulphate (Fig. 8.16). The resulting acid mixture is then heated with excess of sodium hydroxide. The liberated ammonia gas is absorbed in an excess of standard solution of sulphuric acid. The amount of ammonia produced is determined by estimating the amount of sulphuric acid consumed in the reaction. It is done by estimating unreacted sulphuric acid left after the absorption of ammonia by titrating it with standard alkali solution. The difference between the initial amount of acid

288 chemistry taken and that left after the reaction gives the amount of acid reacted with ammonia. Organic compound + H2SO4 ⎯→ (NH4) 2SO4 Na2SO4 + 2NH3 + 2H2O 2NH3 + H2SO4 ⎯→ (NH4) 2SO4 Let the mass of organic compound taken = m g Volume of H2SO4 of molarity, M, taken = V mL Volume of NaOH of molarity, M, used for titration of excess of H2SO4 = V1 mL V1mL of NaOH of molarity M = V1 /2 mL of H2SO4 of molarity M Volume of H2SO4 of molarity M unused = (V - V1/2) mL (V- V1/2) mL of H2SO4 of molarity M = 2(V-V1/2) mL of NH3 solution of molarity M. 1000 mL of 1 M NH3 solution contains 17g NH3 or 14 g of N 2(V-V1/2) mL of NH3 solution of molarity M contains: 1 14 M 2(V V / 2) g N 1000 ×× − 1 14 M 2(V V / 2) 100 Percentage of N 1000 1.4 M 2 (V V / 2) m m ×× − = × ×× − = Kjeldahl method is not applicable to compounds containing nitrogen in nitro and azo groups and nitrogen present in the ring (e.g. pyridine) as nitrogen of these compounds does not change to ammonium sulphate under these conditions. Problem 8.22 During estimation of nitrogen present in an organic compound by Kjeldahl's method, the ammonia evolved from 0.5 g of the compound in Kjeldahl's estimation of nitrogen, neutralized 10 mL of 1 M H2SO4. Find out the percentage of nitrogen in the compound. Solution 1 M of 10 mL H2SO4=1M of 20 mL NH3 1000 mL of 1M ammonia contains 14 g nitrogen 20 mL of 1M ammonia contains Fig.8.16 Kjeldahl method. Nitrogen-containing compound is treated with concentrated H2SO4 to get ammonium sulphate which liberates ammonia on treating with NaOH; ammonia is absorbed in known volume of standard acid.

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14 20 1000 × g nitrogen 14×20×100 Percentage of nitrogen = 56.0% 1000×0.5 = 8.10.3 Halogens Carius method: A known mass of an organic compound is heated with fuming nitric acid in the presence of silver nitrate contained in a hard glass tube known as Carius tube, (Fig.8.17) Percentage of halogen 1 atomic mass of X m g molecular mass of AgX × = Problem 8.23 In Carius method of estimation of halogen, 0.15 g of an organic compound gave 0.12 g of AgBr. Find out the percentage of bromine in the compound. Solution Molar mass of AgBr = 108 + 80 = 188 g mol-1 188 g AgBr contains 80 g bromine 0.12 g AgBr contains 80 0.12 × g 188 g bromine × × = = 80 0.12 100 Percentage of bromine 188×0.15 34.04% 8.10.4 Sulphur A known mass of an organic compound is heated in a Carius tube with sodium peroxide or fuming nitric acid. Sulphur present in the compound is oxidised to sulphuric acid. It is precipitated as barium sulphate by adding excess of barium chloride solution in water. The precipitate is filtered, washed, dried and weighed. The percentage of sulphur can be calculated from the mass of barium sulphate. Let the mass of organic compound taken = m g and the mass of barium sulphate formed = m1g 1 mol of BaSO4 = 233 g BaSO4 = 32 g sulphur m1 g BaSO4 contains 32 100 1

233 m m × × × g sulphur 32 100 1 Percentage of sulphur 233 m m × × = × Fig. 8.17 Carius method. Halogen containing organic compound is heated with fuming nitric acid in the presence of silver nitrate. in a furnace. Carbon and hydrogen present in the compound are oxidised to carbon dioxide and water. The halogen present forms the corresponding silver halide (AgX). It is filtered, washed, dried and weighed. Let the mass of organic compound taken = m g Mass of AgX formed = m1 g 1 mol of AgX contains 1 mol of X Mass of halogen in m1g of AgX 1 atomic mass of X m g molecular mass of AgX × = Problem 8.24 In sulphur estimation, 0.157 g of an organic compound gave 0.4813 g of Rationalised 2023-24 290 chemistry percentage composition (100) and the sum of the percentages of all other elements. However, oxygen can also be estimated directly as follows: A definite mass of an organic compound is decomposed by heating in a stream of nitrogen gas. The mixture of gaseous products containing oxygen is passed over red-hot coke when all the oxygen is converted to carbon monoxide. This mixture is passed through warm iodine pentoxide (I2O5) when carbon monoxide is oxidised to carbon dioxide producing iodine. Compound ⎯ → ⎯⎯heat O2 + other gaseous products 2C + O2 ⎯ → ⎯⎯⎯ 1373 K 2CO]× 5 (A) I2O5 + 5CO ⎯→ I2 + 5CO2]× 2 (B) On making the amount of CO produced in equation (A) equal to the amount of CO used in equation (B) by multiplying the equations (A) and (B) by 5 and 2 respectively; we find that each mole of oxygen liberated from the compound will produce two moles of carbondioxide. Thus 88 g carbon dioxide is obtained if 32 g oxygen is liberated. Let the mass of organic compound taken be m g Mass of carbon dioxide produced be m1 g ∴ m1 g carbon dioxide is obtained from 1 2 32 g O 88 × m ∴Percentage of oxygen = 32 100 1 % 88 m m × × × The percentage of oxygen can be derived from the amount of iodine produced also. Presently, the estimation of elements in an organic compound is carried out by using microquantities of substances and automatic experimental techniques. The elements, carbon, hydrogen and nitrogen present in a compound are determined by an apparatus known as CHN elemental analyser. The analyser requires only a very small amount of the substance (1-3 mg) and displays the values on a screen within a short time. A detailed discussion of such methods is beyond the scope of this book. barium sulphate. What is the percentage of sulphur in the compound? Solution Molecular mass of BaSO4 = 137+32+64 = 233 g 233 g BaSO4 contains 32 g sulphur 0.4813 g BaSO4 contains 32 0.4813 g 233 × g sulphur 32 0.4813 100 Percentage of sulphur 233 0.157 42.10% × × = × = 8.10.5 Phosphorus A known mass of an organic compound is heated with fuming nitric acid whereupon phosphorus present in the compound is oxidised to phosphoric acid. It is precipitated as ammonium phosphomolybdate, (NH4) 3 PO4.12MoO3, by adding ammonia and ammonium molybdate. Alternatively, phosphoric acid may be precipitated as MgNH4PO4 by adding magnesia mixture which on ignition yields Mg2P2O7. Let the mass of organic compound taken = m g and mass of ammonium phospho molydate = m1g Molar mass of (NH4) 3PO4.12MoO3 = 1877g Percentage of phosphorus 31 100 1 % 1877 m m × × = × If phosphorus is estimated as Mg2P2O7, Percentage of phosphorus 62 100 1 % 222 × × m = × where, 222 u is the molar mass of Mg2P2O7, m, the mass of organic compound taken, m1, the mass of Mg2P2O7 formed and 62, the mass of two phosphorus atoms present in the compound Mg2P2O7. 8.10.6 Oxygen The percentage of oxygen in an organic compound is usually found by difference between the total Rationalised 2023-24 organic chemistry – some basic principles and techniques 291 Summary In this unit, we have learnt some basic concepts in structure and reactivity of organic compounds, which are formed due to covalent bonding. The nature of the covalent bonding in organic compounds can be described in terms of orbitals hybridisation concept, according to which carbon can have sp3, sp2 and sp hybridised orbitals. The sp3, sp2 and sp hybridised carbons are found in compounds like methane, ethene and ethyne respectively. The tetrahedral shape of methane, planar shape of ethene and linear shape of ethyne can be understood on the basis of this concept. A sp3 hybrid orbital can overlap with 1s orbital of hydrogen to give a carbon - hydrogen (C–H) single bond (sigma, σ bond). Overlap of a sp2 orbital of one carbon with sp2 orbital of another results in the formation of a carbon–carbon σ bond. The

unhybridised p orbitals on two adjacent carbons can undergo lateral (sideby-side) overlap to give a pi (π) bond. Organic compounds can be represented by various structural formulas. The three dimensional representation of organic compounds on paper can be drawn by wedge and dash formula. Organic compounds can be classified on the basis of their structure or the functional groups they contain. A functional group is an atom or group of atoms bonded together in a unique fashion and which determines the physical and chemical properties of the compounds. The naming of the organic compounds is carried out by following a set of rules laid down by the International Union of Pure and Applied Chemistry (IUPAC). In IUPAC nomenclature, the names are correlated with the structure in such a way that the reader can deduce the structure from the name. Organic reaction mechanism concepts are based on the structure of the substrate molecule, fission of a covalent bond, the attacking reagents, the electron displacement effects and the conditions of the reaction. These organic reactions involve breaking and making of covalent bonds. A covalent bond may be cleaved in heterolytic or homolytic fashion. A heterolytic cleavage yields carbocations or carbanions, while a homolytic cleavage gives free radicals as reactive intermediate. Reactions proceeding through heterolytic cleavage involve the complimentary pairs of reactive species. These are electron pair donor known as nucleophile and an electron pair acceptor known as electrophile. The inductive, resonance, electromeric and hyperconjugation effects may help in the polarisation of a bond making certain carbon atom or other atom positions as places of low or high electron densities. Organic reactions can be broadly classified into following types; substitution, addition, elimination and rearrangement reactions. Purification, qualitative and quantitative analysis of organic compounds are carried out for determining their structures. The methods of purification namely : sublimation, distillation and differential extraction are based on the difference in one or more physical properties. Chromatography is a useful technique of separation, identification and purification of compounds. It is classified into two categories : adsorption and partition chromatography. Adsorption chromatography is based on differential adsorption of various components of a mixture on an adsorbent. Partition chromatography involves continuous partitioning of the components of a mixture between stationary and mobile phases. After getting the compound in a pure form, its qualitative analysis is carried out for detection of elements present in it. Nitrogen, sulphur, halogens and phosphorus are detected by Lassaigne's test. Carbon and hydrogen are estimated by determining the amounts of carbon dioxide and water produced. Nitrogen is estimated by Dumas or Kjeldahl's method and halogens by Carius method. Sulphur and phosphorus are estimated by oxidising them to sulphuric and phosphoric acids respectively. The percentage of oxygen is usually determined by difference between the total percentage (100) and the sum of percentages of all other elements present. Rationalised 2023-24 292 chemistry Exercises 8.1 What are hybridisation states of each carbon atom in the following compounds ? CH2=C=O, CH3CH=CH2, (CH3) 2CO, CH2=CHCN, C6H6 8.2 Indicate the σ and π bonds in the following molecules : C6H6, C6H12, CH2Cl2, CH2=C=CH2, CH3NO2, HCONHCH3 8.3 Write bond line formulas for : Isopropyl alcohol, 2,3-Dimethylbutanal, Heptan-4-one. 8.4 Give the IUPAC names of the following compounds : (a) (b) (c) (d) (e) (f) Cl2CHCH2OH 8.5 Which of the following represents the correct IUPAC name for the compounds concer ned ? (a) 2,2-Dimethylpentane or 2-Dimethylpentane (b) 2,4,7-Trimethyloctane or 2,5,7-Trimethyloctane (c) 2-Chloro-4-methylpentane or 4-Chloro-2-methylpentane (d) But-3-yn-1-ol or But-4-ol-1-yne. 8.6 Draw formulas for the first five members of each homologous series beginning with the following compounds. (a) H–COOH (b) CH3COCH3 (c) H–CH=CH2 8.7 Give condensed and bond line structural formulas and identify the functional group(s) present, if any, for : (a) 2,2,4-Trimethylpentane (b) 2-Hydroxy-1,2,3-propanetricarboxylic acid (c) Hexanedial 8.8 Identify the functional groups in the following compounds (a) (b) (c) 8.9 Which of the two: O2NCH2CH2O– or CH3CH2O– is expected to be more stable and why? 8.10 Explain why alkyl groups act as electron donors when attached to a π system. 8.11 Draw the resonance structures for the following compounds. Show the electron shift

using curved-arrow notation. (a) $C_6H_5OH$ (b) $C_6H_5NO_2$ (c) $CH_3CH=CHCHO$ (d) $C_6H_5–CHO$ (e) $C_6H_5–C^+ H_2$ (f) $CH_3CH=CH\ C^+ H_2$ 8.12 What are electrophiles and nucleophiles ? Explain with examples. 8.13 Identify the reagents shown in bold in the following equations as nucleophiles or electrophiles: (a) $CH_3COOH + HO^- \rightarrow CH_3COO^- + H_2O$ Rationalised 2023-24 organic chemistry – some basic principles and techniques 293 (b) $CH_3COCH_3 + C – N \rightarrow (CH_3)_2C(CN)(OH)$ (c) $C_6H_6 + CH_3C^+ O \rightarrow C_6H_5COCH_3$ 8.14 Classify the following reactions in one of the reaction type studied in this unit. (a) $CH_3CH_2Br + HS^- \rightarrow CH_3CH_2SH + Br^-$ (b) $(CH_3)_2C = CH_2 + HCl \rightarrow (CH_3)_2ClC – CH_3$ (c) $CH_3CH_2Br + HO^- \rightarrow CH_2 = CH_2 + H_2O + Br^-$ (d) $(CH_3)_3C– CH_2OH + HBr \rightarrow (CH_3)_2CBrCH_2CH_2CH_3 + H_2O$ 8.15 What is the relationship between the members of following pairs of structures ? Are they structural or geometrical isomers or resonance contributors ? (a) (b) (c) 8.16 For the following bond cleavages, use curved-arrows to show the electron flow and classify each as homolysis or heterolysis. Identify reactive intermediate produced as free radical, carbocation and carbanion. (a) (b) (c) (d) 8.17 Explain the terms Inductive and Electromeric effects. Which electron displacement effect explains the following correct orders of acidity of the carboxylic acids? (a) $Cl_3CCOOH > Cl_2CHCOOH > ClCH_2COOH$ (b) $CH_3CH_2COOH > (CH_3)_2CHCOOH > (CH_3)_3C.COOH$ 8.18 Give a brief description of the principles of the following techniques taking an example in each case. (a) Crystallisation (b) Distillation (c) Chromatography 8.19 Describe the method, which can be used to separate two compounds with different solubilities in a solvent S. 8.20 What is the difference between distillation, distillation under reduced pressure and steam distillation ? Rationalised 2023-24 294 chemistry 8.21 Discuss the chemistry of Lassaigne's test. 8.22 Differentiate between the principle of estimation of nitrogen in an organic compound by (i) Dumas method and (ii) Kjeldahl's method. 8.23 Discuss the principle of estimation of halogens, sulphur and phosphorus present in an organic compound. 8.24 Explain the principle of paper chromatography. 8.25 Why is nitric acid added to sodium extract before adding silver nitrate for testing halogens? 8.26 Explain the reason for the fusion of an organic compound with metallic sodium for testing nitrogen, sulphur and halogens. 8.27 Name a suitable technique of separation of the components from a mixture of calcium sulphate and camphor. 8.28 Explain, why an organic liquid vaporises at a temperature below its boiling point in its steam distillation ? 8.29 Will $CCl_4$ give white precipitate of AgCl on heating it with silver nitrate? Give reason for your answer. 8.30 Why is a solution of potassium hydroxide used to absorb carbon dioxide evolved during the estimation of carbon present in an organic compound? 8.31 Why is it necessary to use acetic acid and not sulphuric acid for acidification of sodium extract for testing sulphur by lead acetate test? 8.32 An organic compound contains 69% carbon and 4.8% hydrogen, the remainder being oxygen. Calculate the masses of carbon dioxide and water produced when 0.20 g of this substance is subjected to complete combustion. 8.33 A sample of 0.50 g of an organic compound was treated according to Kjeldahl's method. The ammonia evolved was absorbed in 50 ml of 0.5 M $H_2SO_4$. The residual acid required 60 mL of 0.5 M solution of NaOH for neutralisation. Find the percentage composition of nitrogen in the compound. 8.34 0.3780 g of an organic chloro compound gave 0.5740 g of silver chloride in Carius estimation. Calculate the percentage of chlorine present in the compound. 8.35 In the estimation of sulphur by Carius method, 0.468 g of an organic sulphur compound afforded 0.668 g of barium sulphate. Find out the percentage of sulphur in the given compound. 8.36 In the organic compound $CH_2 = CH – CH_2 – CH_2 – C \equiv CH$, the pair of hydridised orbitals involved in the formation of: C2 – C3 bond is: (a) $sp – sp^2$ (b) $sp – sp^3$ (c) $sp^2 – sp^3$ (d) $sp^3 – sp^3$ 8.37 In the Lassaigne's test for nitrogen in an organic compound, the Prussian blue colour is obtained due to the formation of: (a) $Na_4[Fe(CN)_6]$ (b) $Fe_4[Fe(CN)_6]_3$ (c) $Fe_2[Fe(CN)_6]$ (d) $Fe_3[Fe(CN)_6]_4$ 8.38 Which of the following carbocation is most stable ? (a) $(CH_3)_3C. C^+ H_2$ (b) $(CH_3)_3C^+$ (c) $CH_3CH_2C^+ H_2$ (d) $CH_3C^+ H CH_2CH_3$ 8.39 The best and latest technique for isolation, purification and separation of organic compounds is: (a) Crystallisation (b) Distillation (c) Sublimation (d) Chromatography 8.40 The reaction: $CH_3CH_2I + KOH(aq) \rightarrow CH_3CH_2OH + KI$ is classified as : (a)

electrophilic substitution (b) nucleophilic substitution (c) elimination (d) addition After studying this unit, you will be able to • name hydrocarbons according to IUPAC system of nomenclature; • recognise and write structures of isomers of alkanes, alkenes, alkynes and aromatic hydrocarbons; • learn about various methods of preparation of hydrocarbons; • distinguish between alkanes, alkenes, alkynes and aromatic hydrocarbons on the basis of physical and chemical properties; • draw and differentiate between various conformations of ethane; • appreciate the role o f hydrocarbons as sources of energy and for other industrial applications; • predict the formation of the addition products of unsymmetrical alkenes and alkynes on the basis of electronic mechanism; • comprehend the structure of benzene, explain aromaticity and understand mechanism of electrophilic substitution reactions of benzene; • predict the directive influence of substituents in monosubstituted benzene ring; • learn about carcinogenicity and toxicity. Hydrocarbons The term 'hydrocarbon' is self-explanatory which means compounds of carbon and hydrogen only. Hydrocarbons play a key role in our daily life. You must be familiar with the terms 'LPG' and 'CNG' used as fuels. LPG is the abbreviated form of liquified petroleum gas whereas CNG stands for compressed natural gas. Another term 'LNG' (liquified natural gas) is also in news these days. This is also a fuel and is obtained by liquifaction of natural gas. Petrol, diesel and kerosene oil are obtained by the fractional distillation of petroleum found under the earth's crust. Coal gas is obtained by the destructive distillation of coal. Natural gas is found in upper strata during drilling of oil wells. The gas after compression is known as compressed natural gas. LPG is used as a domestic fuel with the least pollution. Kerosene oil is also used as a domestic fuel but it causes some pollution. Automobiles need fuels like petrol, diesel and CNG. Petrol and CNG operated automobiles cause less pollution. All these fuels contain mixture of hydrocarbons, which are sources of energy. Hydrocarbons are also used for the manufacture of polymers like polythene, polypropene, polystyrene etc. Higher hydrocarbons are used as solvents for paints. They are also used as the starting materials for manufacture of many dyes and drugs. Thus, you can well understand the importance of hydrocarbons in your daily life. In this unit, you will learn more about hydrocarbons.

9.1 CLASSIFICATION Hydrocarbons are of different types. Depending upon the types of carbon-carbon bonds present, they can be classified into three main categories – (i) saturated Hydrocarbons are the important sources of energy. (ii) unsaturated and (iii) aromatic hydrocarbons. Saturated hydrocarbons contain carbon-carbon and carbon-hydrogen single bonds. If different carbon atoms are joined together to form open chain of carbon atoms with single bonds, they are termed as alkanes as you have already studied in Unit 8. On the other hand, if carbon atoms form a closed chain or a ring, they are termed as cycloalkanes. Unsaturated hydrocarbons contain carbon-carbon multiple bonds – double bonds, triple bonds or both. Aromatic hydrocarbons are a special type of cyclic compounds. You can construct a large number of models of such molecules of both types (open chain and close chain) keeping in mind that carbon is tetravalent and hydrogen is monovalent. For making models of alkanes, you can use toothpicks for bonds and plasticine balls for atoms. For alkenes, alkynes and aromatic hydrocarbons, spring models can be constructed. 9.2 ALKANES As already mentioned, alkanes are saturated open chain hydrocarbons containing carbon - carbon single bonds. Methane ($CH_4$) is the first member of this family. Methane is a gas found in coal mines and marshy places. If you replace one hydrogen atom of methane by carbon and join the required number of hydrogens to satisfy the tetravalence of the other carbon atom, what do you get? You get $C_2H_6$. This hydrocarbon with molecular formula $C_2H_6$ is known as ethane. Thus you can consider $C_2H_6$ as derived from $CH_4$ by replacing one hydrogen atom by $-CH_3$ group. Go on constructing alkanes by doing this theoretical exercise i.e., replacing hydrogen atom by $-CH_3$ group. The next molecules will be $C_3H_8$, $C_4H_{10}$ ... of the general formula for alkane family or homologous series? If we examine the formula of different alkanes we find that the general formula for alkanes is $C_nH_{2n+2}$. It represents any particular homologue when n is given appropriate value.

Can you recall the structure of methane? According to VSEPR theory (Unit 4), methane has a tetrahedral structure (Fig. 9.1), in which carbon atom lies at the centre and the four hydrogen atoms lie at the four corners of a regular tetrahedron. All H-C-H bond angles are of 109.5°. In alkanes, tetrahedra are joined together in which C-C and C-H bond lengths are 154 pm and 112 pm respectively (Unit 8). You have already read that C–C and C–H σ bonds are formed by head-on overlapping of sp 3 hybrid orbitals of carbon and 1s orbitals of hydrogen atoms. 9.2.1 Nomenclature and Isomerism You have already read about nomenclature of different classes of organic compounds in Unit 8. Nomenclature and isomerism in alkanes can further be understood with the help of a few more examples. Common names are given in parenthesis. First three alkanes – methane, ethane and propane have only one structure but higher alkanes can have more than one structure. Let us write structures for C4H10. Four carbon atoms of C4H10 can be joined either in a continuous chain or with a branched chain in the following two ways : Fig. 9.1 Structure of methane Butane (n- butane), (b.p. 273 K) I H H H H—C—H replace any H by - CH3 H—C—C—H or C2H6 H H H These hydrocarbons are inert under normal conditions as they do not react with acids, bases and other reagents. Hence, they were earlier known as paraffins (latin : parum, little; affinis, affinity). Can you think Rationalised 2023-24 Hydrocarbons 297 In how many ways, you can join five carbon atoms and twelve hydrogen atoms of C5H12? They can be arranged in three ways as shown in structures III–V isomers. It is also clear that structures I and III have continuous chain of carbon atoms but structures II, IV and V have a branched chain. Such structural isomers which differ in chain of carbon atoms are known as chain isomers. Thus, you have seen that C4H10 and C5H12 have two and three chain isomers respectively. Problem 9.1 Write structures of different chain isomers of alkanes corresponding to the molecular formula C6H14. Also write their IUPAC names. Solution (i) CH3 – CH2 – CH2 – CH2– CH2– CH3 n- Hexane 2-Methylpentane 3-Methylpentane 2,3-Dimethylbutane 2,2 - Dimethylbutane Based upon the number of carbon atoms attached to a carbon atom, the carbon atom is termed as primary (1°), secondary (2°), tertiary (3°) or quaternary (4°). Carbon atom attached to no other carbon atom as in methane or to only one carbon atom as in ethane is called primary carbon atom. Terminal carbon atoms are always primary. Carbon atom attached to two carbon atoms is known as secondary. Tertiary carbon is attached to three carbon atoms and neo or quaternary carbon is attached to four carbon atoms. Can you identify 1°, 2°, 3° and 4° carbon atoms in II 2-Methylpropane (isobutane) (b.p.261 K) Structures I and II possess same molecular formula but differ in their boiling points and other properties. Similarly structures III, IV and V possess the same molecular formula but have different properties. Structures I and II are isomers of butane, whereas structures III, IV and V are isomers of pentane. Since difference in properties is due to difference in their structures, they are known as structural III Pentane (n-pentane) (b.p. 309 K) 2-Methylbutane (isopentane) (b.p. 301 K) IV 2,2-Dimethylpropane (neopentane) (b.p. 282.5 K) V Rationalised 2023-24 298 chemistry structures I to V ? If you go on constructing structures for higher alkanes, you will be getting still larger number of isomers. C6H14 has got five isomers and C7H16 has nine. As many as 75 isomers are possible for C10H22. In structures II, IV and V, you observed that –CH3 group is attached to carbon atom numbered as 2. You will come across groups like –CH3, –C2H5, –C3H7 etc. attached to carbon atoms in alkanes or other classes of compounds. These groups or substituents are known as alkyl groups as they are derived from alkanes by removal of one hydrogen atom. General formula for alkyl groups is CnH2n+1 (Unit 8). Let us recall the general rules for nomenclature already discussed in Unit 8. Nomenclature of substituted alkanes can further be understood by considering the following problem: Problem 9.2 Write structures of different isomeric alkyl groups corresponding to the molecular formula C5H11. Write IUPAC names of alcohols obtained by attachment of –OH groups at different carbons of the chain. Solution Structures of – C5H11 group Corresponding alcohols Name of alcohol (i) CH3 – CH2 – CH2 – CH2– CH2 – CH3 – CH2 – CH2 – CH2– CH2 – OH Pentan-1-ol (ii) CH3 – CH – CH2 – CH2 – CH3 CH3 – CH – CH2 – CH2– CH3 Pentan-2-ol | | OH (iii) CH3 – CH2 – CH – CH2 –

CH3 CH3 – CH2 – CH – CH2– CH3 Pentan-3-ol | | OH CH3 CH3 3-Methyl- | | butan-1-ol (iv) CH3 – CH – CH2 – CH2 – CH3 – CH – CH2 – CH2– OH CH3 CH3 2-Methyl- | | butan-1-ol (v) CH3 – CH2 – CH – CH2 – CH3 – CH2 – CH2– OH CH3 CH3 2-Methyl- | | butan-2-ol (vi) CH3 – C – CH2 – CH3 CH3 – C – CH2 – CH3 | | OH CH3 CH3 2,2- Dimethyl- | | propan-1-ol (vii) CH3 – C – CH2 – CH3 – C – CH2OH | | CH3 CH3 CH3 CH3 OH 3-Methyl- | | | | butan-2-ol (viii) CH3 – CH – CH –CH3 CH3 – CH – CH –CH3 Rationalised 2023-24 Hydrocarbons 299 Remarks Lowest sum and alphabetical arrangement Lowest sum and alphabetical arrangement sec is not considered while arranging alphabetically; isopropyl is taken as one word Further numbering to the substituents of the side chain Alphabetical priority order Table 9.1 Nomenclature of a Few Organic Compounds important to write the correct structure from the given IUPAC name. To do this, first of all, the longest chain of carbon atoms corresponding to the parent alkane is written. Then after numbering it, the substituents are attached to the correct carbon atoms and finally valence of each carbon atom is satisfied by putting the correct number of hydrogen atoms. This can be clarified by writing the structure of 3-ethyl-2, 2–dimethylpentane in the following steps : i) Draw the chain of five carbon atoms: C – C – C – C – C ii) Give number to carbon atoms: C1 – C2 – C3 – C4 – C5 Structure and IUPAC Name (a) 1 CH3– 2 CH – 3 CH2 – 4 CH – 5 CH2 – 6 CH3 (4 – Ethyl – 2 – methylhexane) (b) 8 CH3 – 7CH2 – 6CH2 – 5CH – 4CH – 3C – 2CH2 – 1CH3 (3,3-Diethyl-5-isopropyl-4-methyloctane) (c) 1 CH3– 2 CH2– 3 CH2– 4 CH–5 CH–6 CH2– 7 CH2– 8 CH2– 9 CH2– 10CH3 5-sec– Butyl-4-isopropyldecane (d) 1 CH3– 2 CH2– 3 CH2– 4 CH2– 5 CH–6 CH2– 7 CH2– 8 CH2– 9 CH3 5-(2,2– Dimethylpropyl)nonane (e) 1 CH3 – 2CH2 – 3CH – 4CH2 – 5CH – 6CH2 – 7CH3 3–Ethyl–5–methylheptane Problem 9.3 Write IUPAC names of the following compounds : (i) (CH3) 3 C CH2C(CH3) 3 (ii) (CH3) 2 C(C2H5) 2 (iii) tetra – tert-butylmethane Solution (i) 2, 2, 4, 4-Tetramethylpentane (ii) 3, 3-Dimethylpentane (iii) 3,3-Di-tert-butyl -2, 2, 4, 4 - tetramethylpentane If it is important to write the correct IUPAC name for a given structure, it is equally Rationalised 2023-24 300 chemistry iii) Attach ethyl group at carbon 3 and two methyl groups at carbon 2 C1 – 2 C – 3 C – 4 C – 5 C iv) Satisfy the valence of each carbon atom by putting requisite number of hydrogen atoms : CH3 – C – CH – CH2 – CH3 Thus we arrive at the correct structure. If you have understood writing of structure from the given name, attempt the following problems. Problem 9.4 Write structural formulas of the following compounds : (i) 3, 4, 4, 5–Tetramethylheptane (ii) 2,5-Dimethyhexane Solution (i) CH3 – CH2 – CH – C – CH– CH – CH3 (ii) CH3 – CH – CH2– CH2 – CH – CH3 Problem 9.5 Write structures for each of the following compounds. Why are the given names incorrect? Write correct IUPAC names. (i) 2-Ethylpentane (ii) 5-Ethyl – 3-methylheptane Solution (i) CH3 – CH – CH2– CH2 – CH3 Longest chain is of six carbon atoms and not that of five. Hence, correct name is 3-Methylhexane. 7 6 5 4 3 2 1 (ii) CH3 – CH2 – CH – CH2 – CH – CH2 – CH3 Numbering is to be started from the end which gives lower number to ethyl group. Hence, correct name is 3-ethyl-5-methylheptane. 9.2.2 Preparation Petroleum and natural gas are the main sources of alkanes. However, alkanes can be prepared by following methods : 1. From unsaturated hydrocarbons Dihydrogen gas adds to alkenes and alkynes in the presence of finely divided catalysts like platinum, palladium or nickel to form alkanes. This process is called hydrogenation. These metals adsorb dihydrogen gas on their surfaces and activate the hydrogen – hydrogen bond. Platinum and palladium catalyse the reaction at room temperature but relatively higher temperature and pressure are required with nickel catalysts. CH2 =CH2 + H2 Pt/Pd/Ni CH3–CH3 Ethene Propane (9.1) CH2–CH=CH2 + H2 Pt/Pd/Ni CH3–CH2CH3 Propane Propane (9.2) CH3–C≡ C–H + 2H Pt/Pd/Ni CH3–CH2CH3 Propyne Propane (9.3) 2. From alkyl halides i) Alkyl halides (except fluorides) on reduction with zinc and dilute hydrochloric acid give alkanes. CH–C1+H2 Zn,H+ CH4+HC1 (9.4) Chloromethane Methane Rationalised 2023-24 Hydrocarbons 301 C2H5–C1+H2 Zn,H+ C2H6+HC1 Chloroethane Ethane (9.5) CH3CH2CH2C1 + H2 Zn,H+ CH3CH2CH3+CH1 1-Chloropropane Propane (9.6) ii) Alkyl halides on treatment with sodium metal in dry ethereal (free from moisture) solution give higher alkanes. This reaction is known as Wurtz reaction and is used for the preparation of

higher alkanes containing even number of carbon atoms. $CH_3Br+2Na+BrCH_3$ dry ether $CH_3+2Na$ Bromomenthane Ethane (9.7) $C_2H_5br+2Na+BrC_2H_5$ dry ether $C_2H_5–C_2H$ Bromoethane n–Butane (9.8) What will happen if two different alkyl halides are taken? 3. From carboxylic acids i) Sodium salts of carboxylic acids on heating with soda lime (mixture of sodium hydroxide and calcium oxide) give alkanes containing one carbon atom less than the carboxylic acid. This process of elimination of carbon dioxide from a carboxylic acid is known as decarboxylation. $CH_3COO^- Na^+ +MaOH$ Δ CaO $CH_4+NaCO_3$ Sodium ethanoate Problem 9.6 Sodium salt of which acid will be needed for the preparation of propane ? Write chemical equation for the reaction. Solution Butanoic acid, $CH_3CH_2CH_2COO^- Na^+$ + NaOH CaO $CH_3CH_2CH_3+Na_2CO_3$ ii) Kolbe's electrolytic method An aqueous solution of sodium or potassium salt of a carboxylic acid on electrolysis gives alkane containing even number of carbon atoms at the anode. $+ 3\ 2\ 3\ 3\ 22$ Electrolysts $2CH\ COO\ Na\ 2H\ O$ Sodium acetate CH CH $2CO\ H\ 2NaOH − +\ ↓\ −\ +\ ++$ (9.9) The reaction is supposed to follow the following path : O i) $2CH_3COO^- Na^+\ 2CH_3 – C – O– +2Na+$ ii) At anode: O O $2CH_3 –C–O– –02e–\ 2CH_3–C– 2C. H_3+2CO_2↑$ Acetate ion Acetate Methyl free free radical radical iii) $H_3C + CH_3\ H_3C–CH_3↑$ iv) At cathode : $H_2O+e–→–OH+ 2 →H_2↑$ Methane cannot be prepared by this method. Why? 9.2.3 Properties Physical properties Alkanes are almost non-polar molecules because of the covalent nature of C-C and C-H bonds and due to very little difference of electronegativity between carbon and hydrogen atoms. They possess weak van der Waals forces. Due to the weak forces, the first four members, C1 to C4 are gases, C5 to C17 are liquids and those containing 18 carbon atoms or more are solids at 298 K. They are colourless and odourless. What do you think about solubility of alkanes in water based upon non-polar nature of alkanes? Petrol is a mixture of hydrocarbons and is used as a fuel for automobiles. Petrol and lower fractions of petroleum are also used for dry cleaning of clothes to remove grease stains. On the basis of this observation, what do you think about the nature of the greasy substance? You are correct if you say that grease (mixture of higher alkanes) is nonRationalised 2023-24 302 chemistry polar and, hence, hydrophobic in nature. It is generally observed that in relation to solubility of substances in solvents, polar substances are soluble in polar solvents, whereas the non-polar ones in non-polar solvents i.e., like dissolves like. Boiling point (b.p.) of different alkanes are given in Table 9.2 from which it is clear that there is a steady increase in boiling point with increase in molecular mass. This is due to the fact that the intermolecular van der Waals forces increase with increase of the molecular size or the surface area of the molecule. You can make an interesting observation by having a look on the boiling points of three isomeric pentanes viz., (pentane, 2-methylbutane and 2,2-dimethylpropane). It is observed (Table 9.2) that pentane having a continuous chain of five carbon atoms has the highest boiling point (309.1K) whereas 2,2 – dimethylpropane boils at 282.5K. With increase in number of branched chains, the molecule attains the shape of a sphere. This results in smaller area of contact and therefore weak intermolecular forces between spherical molecules, which are overcome at relatively lower temperatures. Chemical properties As already mentioned, alkanes are generally inert towards acids, bases, oxidising and reducing agents. However, they undergo the following reactions under certain conditions. 1. Substitution reactions One or more hydrogen atoms of alkanes can be replaced by halogens, nitro group and sulphonic acid group. Halogenation takes place either at higher temperature (573-773 K) or in the presence of diffused sunlight or ultraviolet light. Lower alkanes do not undergo nitration and sulphonation reactions. These reactions in which hydrogen atoms of alkanes are substituted are known as substitution reactions. As an example, chlorination of methane is given below: Halogenation $CH_2 + C_1$ hv $CH_3C_1$ + HC1 Chloromethane (9.10) $CH_3C_1$ + hv $CH_2\ C_{12}$ + HC1 Dichloromethane (9.11) $CH_2C_{12}$ hv $CHC_{13}$ + HC1 Trichloromethane (9.12) $CHC_{13} + C_{12}$ hv $CC_{14}$ + HC1 Tetrachloromethane (9.13) Table 9.2 Variation of Melting Point and Boiling Point in Alkanes

| Molecular formula | Name | Molecular mass/u | b.p./(K) | m.p./(K) |
|---|---|---|---|---|
| CH4 | Methane | 16 | 111.0 | 90.5 |
| C2H6 | Ethane | 30 | 184.4 | 101.0 |
| C3H8 | Propane | 44 | 230.9 | 85.3 |
| C4H10 | Butane | 58 | 272.4 | 134.6 |
| C4H10 | 2- | | | |

Methylpropane 58 261.0 114.7 C5H12 Pentane 72 309.1 143.3 C5H12 2-Methylbutane 72 300.9 113.1 C5H12 2,2-Dimethylpropane 72 282.5 256.4 C6H14 Hexane 86 341.9 178.5 C7H16 Heptane 100 371.4 182.4 C8H18 Octane 114 398.7 216.2 C9H20 Nonane 128 423.8 222.0 C10H22 Decane 142 447.1 243.3 C20H42 Eicosane 282 615.0 236.2 Rationalised 2023-24 Hydrocarbons 303 CH3–CH3 + C12 hv CH3–CH2C1 + HC1 Chloroethane (9.14) It is found that the rate of reaction of alkanes with halogens is F2 > Cl2 > Br2 > I2. Rate of replacement of hydrogens of alkanes is : 3° > 2° > 1°. Fluorination is too violent to be controlled. Iodination is very slow and a reversible reaction. It can be carried out in the presence of oxidizing agents like HIO3 or HNO3. CH4+I2 CH3I+HI (9.15) HIO3+5HI→312+3H2O (9.16) Halogenation is supposed to proceed via free radical chain mechanism involving three steps namely initiation, propagation and termination as given below: Mechanism (i) Initiation : The reaction is initiated by homolysis of chlorine molecule in the presence of light or heat. The Cl–Cl bond is weaker than the C–C and C–H bond and hence, is easiest to break. C1–C1 hv homolysis C . H3 + C1 Chlorine free radicals (ii) Propagation : Chlorine free radical attacks the methane molecule and takes the reaction in the forward direction by breaking the C-H bond to generate methyl free radical with the formation of H-Cl. (a) CH4 + C+ 1 hv C + H3 + H–C1 The methyl radical thus obtained attacks the second molecule of chlorine to form CH3 – Cl with the liberation of another chlorine free radical by homolysis of chlorine molecule. (b) CH3 + C1–C1 hv CH3 – C1 + C1 The chlorine and methyl free radicals generated above repeat steps (a) and (b) respectively and thereby setup a chain of reactions. The propagation steps (a) and (b) are those which directly give principal products, but many other propagation steps are possible and may occur. Two such steps given below explain how more highly halogenated products are formed. CH3C1 + C. 1 → C . H2C1 + HC1 C . H2C1 + C1– C1 → CH2C12 + C. 1 (iii) Termination: The reaction stops after some time due to consumption of reactants and / or due to the following side reactions : The possible chain terminating steps are: (a) C . 1 + C. 1 → C1–C1 (b) H3 C . + C. H3 → H3C– CH3 (c) H3 C . 1 + C. 1 → H3C–C1 Though in (c), CH3 – Cl, the one of the products is formed but free radicals are consumed and the chain is terminated. The above mechanism helps us to understand the reason for the formation of ethane as a byproduct during chlorination of methane. 2. Combustion Alkanes on heating in the presence of air or dioxygen are completely oxidized to carbon dioxide and water with the evolution of large amount of heat. 42 2 2 è -1 c 4 10 2 2 2 è -1 c CH (g) 20 (g) CO (g) 2H O(1); Ä H 890kJmol (9.17) C H (g) 13/2O (g) 4CO (g) 5H O(1) Ä H 2875.84kJmol (9.18) +→ + − + →+ = − The general combustion equation for any alkane is : n 2n+2 2 2 2 3n 1 C H O nCO (n 1)H O 2 𝟐 + + → ++ 𝟐 𝟐 𝟐 (9.19) Due to the evolution of large amount of heat during combustion, alkanes are used as fuels. During incomplete combustion of alkanes with insufficient amount of air or dioxygen, carbon black is formed which is used in the manufacture of ink, printer ink, black pigments and as filters. Rationalised 2023-24 304 chemistry CH4(g) + O2(g) incomplete combustion C(s)+2H2 O(1) (9.20) 3. Controlled oxidation Alkanes on heating with a regulated supply of dioxygen or air at high pressure and in the presence of suitable catalysts give a variety of oxidation products. (i) 2CH4 + O2 Cu/523K/100atm 2CH3 OH Methanol (9.21) (ii) CH4 + O2 Mo2O3 Δ HCHO + H2O Methanal (9.22) (iii) 2CH3CH3 + 3O2 (CH3COO)Mn Δ 2CH3COOH Ethanoic acid + 2H2O (9.23) (iv) Ordinarily alkanes resist oxidation but alkanes having tertiary H atom can be oxidized to corresponding alcohols by potassium permanganate. (iCH3) 3 CH KMnO4 Oxidation (CH3) 3 COH 2-Methylpropane 2-Methylpropane-2-01 (9.24) 4. Isomerisation n-Alkanes on heating in the presence of anhydrous aluminium chloride and hydrogen chloride gas isomerise to branched chain alkanes. Major products are given below. Some minor products are also possible which you can think over. Minor products are generally not reported in organic reactions. CH3(CH)2)4CH3 Anhy, AICI3/ HCI n-Hexane CH3CH–(CH2) 2– CH3+CH3CH2–CH–CH2–CH3 CH3 CH3 2-Methylpen tane 3-Methylpenatone (9.25) 5. Aromatization n-Alkanes having six or more carbon atoms on heating to 773K at 10-20 atmospheric pressure in the presence of oxides of vanadium, molybdenum or chromium supported over alumina get

dehydrogenated and cyclised to benzene and its homologues. This reaction is known as aromatization or reforming. (9.26) Toluene ($C_7H_8$) is methyl derivative of benzene. Which alkane do you suggest for preparation of toluene ? 6. Reaction with steam Methane reacts with steam at 1273 K in the presence of nickel catalyst to form carbon monoxide and dihydrogen. This method is used for industrial preparation of dihydrogen gas $CH_4 + H_2O \xrightarrow[\Delta]{Ni} CO + 3H_2$ (9.27) 7. Pyrolysis Higher alkanes on heating to higher temperature decompose into lower alkanes, alkenes etc. Such a decomposition reaction into smaller fragments by the application of heat is called pyrolysis or cracking. (9.28) Pyrolysis of alkanes is believed to be a free radical reaction. Preparation of oil gas or petrol gas from kerosene oil or petrol involves the principle of pyrolysis. For example, dodecane, a constituent of kerosene oil on heating to 973K in the presence of platinum, palladium or nickel gives a mixture of heptane and pentene. $C_{12}H_{26} \xrightarrow[973K]{Pt/Pd/Ni} C_7H_{16} + C_5H_{10}$ Other Products Dodecane Heptane Pentene (9.29) Rationalised 2023-24 Hydrocarbons 305 9.2.4 Conformations Alkanes contain carbon-carbon sigma ($\sigma$) bonds. Electron distribution of the sigma molecular orbital is symmetrical around the internuclear axis of the C–C bond which is not disturbed due to rotation about its axis. This permits free rotation about C–C single bond. This rotation results into different spatial arrangements of atoms in space which can change into one another. Such spatial arrangements of atoms which can be converted into one another by rotation around a C-C single bond are called conformations or conformers or rotamers. Alkanes can thus have infinite number of conformations by rotation around C-C single bonds. However, it may be remembered that rotation around a C-C single bond is not completely free. It is hindered by a small energy barrier of 1-20 kJ mol$^{-1}$ due to weak repulsive interaction between the adjacent bonds. Such a type of repulsive interaction is called torsional strain. Conformations of ethane : Ethane molecule ($C_2H_6$) contains a carbon – carbon single bond with each carbon atom attached to three hydrogen atoms. Considering the ball and stick model of ethane, keep one carbon atom stationary and rotate the other carbon atom around the C-C axis. This rotation results into infinite number of spatial arrangements of hydrogen atoms attached to one carbon atom with respect to the hydrogen atoms attached to the other carbon atom. These are called conformational isomers (conformers). Thus there are infinite number of conformations of ethane. However, there are two extreme cases. One such conformation in which hydrogen atoms attached to two carbons are as closed together as possible is called eclipsed conformation and the other in which hydrogens are as far apart as possible is known as the staggered conformation. Any other intermediate conformation is called a skew conformation.It may be remembered that in all the conformations, the bond angles and the bond lengths remain the same. Eclipsed and the staggered conformations can be represented by Sawhorse and Newman projections. 1. Sawhorse projections In this projection, the molecule is viewed along the molecular axis. It is then projected on paper by drawing the central C–C bond as a somewhat longer straight line. Upper end of the line is slightly tilted towards right or left hand side. The front carbon is shown at the lower end of the line, whereas the rear carbon is shown at the upper end. Each carbon has three lines attached to it corresponding to three hydrogen atoms. The lines are inclined at an angle of 120° to each other. Sawhorse projections of eclipsed and staggered conformations of ethane are depicted in Fig. 9.2. 2. Newman projections In this projection, the molecule is viewed at the C–C bond head on. The carbon atom nearer to the eye is represented by a point. Three hydrogen atoms attached to the front carbon atom are shown by three lines drawn at an angle of 120° to each other. The rear carbon atom (the carbon atom away from the eye) is represented by a circle and the three hydrogen atoms are shown attached to it by the shorter lines drawn at an angle of 120° to each other. The Newman's projections are depicted in Fig. 9.3. Fig. 9.2 Sawhorse projections of ethane Fig. 9.3 Newman's projections of ethane Rationalised 2023-24 306 chemistry Fig. 9.4 Orbital picture of ethene depicting σ bonds only Relative stability of conformations: As mentioned earlier, in staggered form of ethane, the electron clouds of carbon-hydrogen bonds are as far apart as possible. Thus, there are minimum repulsive

forces, minimum energy and maximum stability of the molecule. On the other hand, when the staggered form changes into the eclipsed form, the electron clouds of the carbon – hydrogen bonds come closer to each other resulting in increase in electron cloud repulsions. To check the increased repulsive forces, molecule will have to possess more energy and thus has lesser stability. As already mentioned, the repulsive interaction between the electron clouds, which affects stability of a conformation, is called torsional strain. Magnitude of torsional strain depends upon the angle of rotation about C–C bond. This angle is also called dihedral angle or torsional angle. Of all the conformations of ethane, the staggered form has the least torsional strain and the eclipsed form, the maximum torsional strain. Therefore, staggered conformation is more stable than the eclipsed conformation. Hence, molecule largely remains in staggered conformation or we can say that it is preferred conformation. Thus it may be inferred that rotation around C–C bond in ethane is not completely free. The energy difference between the two extreme forms is of the order of 12.5 kJ mol–1, which is very small. Even at ordinary temperatures, the ethane molecule gains thermal or kinetic energy sufficient enough to overcome this energy barrier of 12.5 kJ mol–1 through intermolecular collisions. Thus, it can be said that rotation about carbon-carbon single bond in ethane is almost free for all practical purposes. It has not been possible to separate and isolate different conformational isomers of ethane. 9.3 Alkenes Alkenes are unsaturated hydrocarbons containing at least one double bond. What should be the general formula of alkenes? If there is one double bond between two carbon atoms in alkenes, they must possess two hydrogen atoms less than alkanes. Hence, general formula for alkenes is $CnH2n$. Alkenes are also known as olefins (oil forming) since the first member, ethylene or ethene ($C2H4$) was found to form an oily liquid on reaction with chlorine. 9.3.1 Structure of Double Bond Carbon-carbon double bond in alkenes consists of one strong sigma (σ) bond (bond enthalpy about 397 kJ mol–1) due to head-on overlapping of sp 2 hybridised orbitals and one weak pi (π) bond (bond enthalpy about 284 kJ mol–1) obtained by lateral or sideways overlapping of the two 2p orbitals of the two carbon atoms. The double bond is shorter in bond length (134 pm) than the C–C single bond (154 pm). You have already read that the pi (π) bond is a weaker bond due to poor sideways overlapping between the two 2p orbitals. Thus, the presence of the pi (π) bond makes alkenes behave as sources of loosely held mobile electrons. Therefore, alkenes are easily attacked by reagents or compounds which are in search of electrons. Such reagents are called electrophilic reagents. The presence of weaker π-bond makes alkenes unstable molecules in comparison to alkanes and thus, alkenes can be changed into single bond compounds by combining with the electrophilic reagents. Strength of the double bond (bond enthalpy, 681 kJ mol–1) is greater than that of a carbon-carbon single bond in ethane (bond enthalpy, 348 kJ mol–1). Orbital diagrams of ethene molecule are shown in Figs. 9.4 and 9.5. 9.3.2 Nomenclature For nomenclature of alkenes in IUPAC system, the longest chain of carbon atoms containing the double bond is selected. Numbering of the chain is done from the end which is nearer to Rationalised 2023-24 Hydrocarbons 307 the double bond. The suffix 'ene' replaces 'ane' of alkanes. It may be remembered that first member of alkene series is: CH2 (replacing n by 1 in $CnH2n$) known as methene but has a very short life. As already mentioned, first stable member of alkene series is $C2H4$ known as ethylene (common) or ethene (IUPAC). IUPAC names of a few members of alkenes are given below : Structure IUPAC name CH3 – CH = CH2 Propene CH3 – CH2 – CH = CH2 But – l - ene CH3 – CH = CH–CH3 But-2-ene CH2 = CH – CH = CH2 Buta – 1,3 - diene CH2 = C – CH3 2-Methylprop-1-ene | CH3 CH2 = CH – CH – CH3 3-Methylbut-1-ene | CH3 Problem 9.7 Write IUPAC names of the following compounds: (i) (CH3) 2CH – CH = CH – CH2 – CH ψ CH3 – CH – CH | C2H5 (ii) (iii) CH2 = C (CH2CH2CH3) 2 (iv) CH3 CH2 CH2 CH2 CH2CH3 | | CH3 – CHCH = C – CH2 – CHCH3 | CH3 Solution (i) 2,8-Dimethyl-3, 6-decadiene; (ii) 1,3,5,7 Octatetraene; (iii) 2-n-Propylpent-1-ene; (iv) 4-Ethyl-2,6-dimethyl-dec-4-ene; Problem 9.8 Calculate number of sigma (σ) and pi (π) bonds in the above structures (i-iv). Solution σ bonds : 33, π bonds : 2 σ bonds : 17, π bonds : 4 σ bonds : 23, π

bond : 1 σ bonds : 41, π bond : 1 9.3.3 Isomerism Alkenes show both structural isomerism and geometrical isomerism. Structural isomerism : As in alkanes, ethene ($C_2H_4$) and propene ($C_3H_6$) can have only one structure but alkenes higher than propene have different structures. Alkenes possessing $C_4H_8$ as molecular formula can be written in the following three ways: I. 1 2 3 4 $CH_2 = CH – CH_2 – CH_3$ But-1-ene ($C_4H_8$) II. 1 2 3 4 $CH_3 – CH = CH – CH_3$ But-2-ene ($C_4H_8$) Fig. 9.5 Orbital picture of ethene showing formation of (a) π-bond, (b) π-cloud and (c) bond angles and bond lengths Rationalised 2023-24 308 chemistry III. 1 2 3 $CH_2 = C – CH_3$ | $CH_3$ 2-Methyprop-1-ene ($C_4H_8$) Structures I and III, and II and III are the examples of chain isomerism whereas structures I and II are position isomers. Problem 9.9 Write structures and IUPAC names of different structural isomers of alkenes corresponding to $C_5H_{10}$. Solution (a) $CH_2 = CH – CH_2 – CH_2 – CH_3$ Pent-1-ene (b) $CH_3 – CH=CH – CH_2 – CH_3$ Pent-2-ene (c) $CH_3 – C = CH – CH_3$ | $CH_3$ 2-Methylbut-2-ene (d) $CH_3 – CH – CH = CH_2$ | $CH_3$ 3-Methylbut-1-ene (e) $CH_2 = C – CH_2 – CH_3$ | $CH_3$ 2-Methylbut-1-ene Geometrical isomerism: Doubly bonded carbon atoms have to satisfy the remaining two valences by joining with two atoms or groups. If the two atoms or groups attached to each carbon atom are different, they can be represented by YX C = C XY like structure. YX C = C XY can be represented in space in the following two ways : In (a), the two identical atoms i.e., both the X or both the Y lie on the same side of the double bond but in (b) the two X or two Y lie across the double bond or on the opposite sides of the double bond. This results in different geometry of (a) and (b) i.e. disposition of atoms or groups in space in the two arrangements is different. Therefore, they are stereoisomers. They would have the same geometry if atoms or groups around C=C bond can be rotated but rotation around C=C bond is not free. It is restricted. For understanding this concept, take two pieces of strong cardboards and join them with the help of two nails. Hold one cardboard in your one hand and try to rotate the other. Can you really rotate the other cardboard ? The answer is no. The rotation is restricted. This illustrates that the restricted rotation of atoms or groups around the doubly bonded carbon atoms gives rise to different geometries of such compounds. The stereoisomers of this type are called geometrical isomers. The isomer of the type (a), in which two identical atoms or groups lie on the same side of the double bond is called cis isomer and the other isomer of the type (b), in which identical atoms or groups lie on the opposite sides of the double bond is called trans isomer . Thus cis and trans isomers have the same structure but have different configuration (arrangement of atoms or groups in space). Due to different arrangement of atoms or groups in space, these isomers differ in their properties like melting point, boiling point, dipole moment, solubility etc. Geometrical or cis-trans isomers of but-2-ene are represented below : Cis form of alkene is found to be more polar than the trans form. For example, dipole moment of cis-but-2-ene is 0.33 Debye, whereas, dipole moment of the trans form is almost zero or it can be said that Rationalised 2023-24 Hydrocarbons 309 trans-but-2-ene is non-polar. This can be understood by drawing geometries of the two forms as given below from which it is clear that in the trans-but-2-ene, the two methyl groups are in opposite directions, Threfore, dipole moments of C-CH3 bonds cancel, thus making the trans form non-polar. (ii) $CH_2 = CBr_2$ (iii) $C_6H_5CH = CH – CH_3$ (iv) $CH_3CH = CCl\ CH_3$ Solution (iii) and (iv). In structures (i) and (ii), two identical groups are attached to one of the doubly bonded carbon atom. 9.3.4 Preparation 1. From alkynes: Alkynes on partial reduction with calculated amount of dihydrogen in the presence of palladised charcoal partially deactivated with poisons like sulphur compounds or quinoline give alkenes. Partially deactivated palladised charcoal is known as Lindlar's catalyst. Alkenes thus obtained are having cis geometry. However, alkynes on reduction with sodium in liquid ammonia form trans alkenes. (9.30) (9.31) iii) $CH≡ CH+H_2$ Pd/C $CH_2 =CH_2$ (9.32) Ethyne Ethene iv) $CH_3–C≡ CH+H_2$ Pd/C $CH_3–CH =CH_2$ Propyne Propene (9.33) Will propene thus obtained show geometrical isomerism? Think for the reason in support of your answer. 2. From alkyl halides: Alkyl halides (R-X) on heating with alcoholic potash (potassium hydroxide dissolved in alcohol, say, In the case of solids, it is observed that the trans isomer has higher melting point than the cis form.

Geometrical or cis-trans isomerism is also shown by alkenes of the types XYC = CXZ and XYC = CZW Problem 9.10 Draw cis and trans isomers of the following compounds. Also write their IUPAC names : (i) CHCl = CHCl (ii) C2H5CCH3 = CCH3C2H5 Solution Problem 9.11 Which of the following compounds will show cis-trans isomerism? (i) (CH3) 2C = CH – C2H5 cis-But-2-ene ($\mu$ = 0.33D) trans-But-2-ene ($\mu$ = 0) Rationalised 2023-24 310 chemistry ethanol) eliminate one molecule of halogen acid to form alkenes. This reaction is known as dehydrohalogenation i.e., removal of halogen acid. This is example of $\beta$-elimination reaction, since hydrogen atom is eliminated from the $\beta$ carbon atom (carbon atom next to the carbon to which halogen is attached). (9.34) Nature of halogen atom and the alkyl group determine rate of the reaction. It is observed that for halogens, the rate is: iodine > bromine > chlorine, while for alkyl groups it is : tert > secondary > primary. 3. From vicinal dihalides: Dihalides in which two halogen atoms are attached to two adjacent carbon atoms are known as vicinal dihalides. Vicinal dihalides on treatment with zinc metal lose a molecule of $ZnX_2$ to form an alkene. This reaction is known as dehalogenation. $CH_2Br–CH_2Br + Zn \rightarrow CH_2=CH_2 + ZnBr_2$ (9.35) $CH_3CHBr–CH_2Br + Zn \rightarrow CH_3CH=CH_2 + ZnBr_2$ (9.36) 4. From alcohols by acidic dehydration: You have read during nomenclature of different homologous series in Unit 12 that alcohols are the hydroxy derivatives of alkanes. They are represented by R–OH where, R is $CnH2n+1$. Alcohols on heating with concentrated sulphuric acid form alkenes with the elimination of one water molecule. Since a water molecule is eliminated from the alcohol molecule in the presence of an acid, this reaction is known as acidic dehydration of alcohols. This reaction is also the example of $\beta$-elimination reaction since –OH group takes out one hydrogen atom from the $\beta$-carbon atom. (9.37) 9.3.5 Properties Physical properties Alkenes as a class resemble alkanes in physical properties, except in types of isomerism and difference in polar nature. The first three members are gases, the next fourteen are liquids and the higher ones are solids. Ethene is a colourless gas with a faint sweet smell. All other alkenes are colourless and odourless, insoluble in water but fairly soluble in non-polar solvents like benzene, petroleum ether. They show a regular increase in boiling point with increase in size i.e., every – CH2 group added increases boiling point by 20–30 K. Like alkanes, straight chain alkenes have higher boiling point than isomeric branched chain compounds. Chemical properties Alkenes are the rich source of loosely held pi ($\pi$) electrons, due to which they show addition reactions in which the electrophiles add on to the carbon-carbon double bond to form the addition products. Some reagents also add by free radical mechanism. There are cases when under special conditions, alkenes also undergo free radical substitution reactions. Oxidation and ozonolysis reactions are also quite prominent in alkenes. A brief description of different reactions of alkenes is given below: 1. Addition of dihydrogen: Alkenes add up one molecule of dihydrogen gas in the presence of finely divided nickel, palladium or platinum to form alkanes (Section 9.2.2) 2. Addition of halogens : Halogens like bromine or chlorine add up to alkene to form vicinal dihalides. However, iodine does not show addition reaction under Rationalised 2023-24 Hydrocarbons 311 normal conditions. The reddish orange colour of bromine solution in carbon tetrachloride is discharged when bromine adds up to an unsaturation site. This reaction is used as a test for unsaturation. Addition of halogens to alkenes is an example of electrophilic addition reaction involving cyclic halonium ion formation which you will study in higher classes. (9.38) (9.39) 3. Addition of hydrogen halides: Hydrogen halides (HCl, HBr,HI) add up to alkenes to form alkyl halides. The order of reactivity of the hydrogen halides is HI > HBr > HCl. Like addition of halogens to alkenes, addition of hydrogen halides is also an example of electrophilic addition reaction. Let us illustrate this by taking addition of HBr to symmetrical and unsymmetrical alkenes Addition reaction of HBr to symmetrical alkenes Addition reactions of HBr to symmetrical alkenes (similar groups attached to double bond) take place by electrophilic addition mechanism. $CH_2=CH_2 + H–Br \rightarrow CH_3–CH_2–Br$ (9.40) $CH_3–CH=CH–CH_3 + HBr \rightarrow CH_3–CH–CHCH_3$ Br (9.41) Addition reaction of HBr to unsymmetrical alkenes (Markovnikov Rule) How will H – Br add to propene ? The two possible products are I and II. (9.42) Markovnikov, a Russian chemist made a

generalisation in 1869 after studying such reactions in detail. These generalisations led Markovnikov to frame a rule called Markovnikov rule. The rule states that negative part of the addendum (adding molecule) gets attached to that carbon atom which possesses lesser number of hydrogen atoms. Thus according to this rule, product I i.e., 2-bromopropane is expected. In actual practice, this is the principal product of the reaction. This generalisation of Markovnikov rule can be better understood in terms of mechanism of the reaction. Mechanism Hydrogen bromide provides an electrophile, H+ , which attacks the double bond to form carbocation as shown below : (i) The secondary carbocation (b) is more stable than the primary carbocation (a), therefore, the former predominates because it is formed at a faster rate. (ii) The carbocation (b) is attacked by Br– ion to form the product as follows : 2-Bromopropane (major product) (a) less stable primary carbocation (b) more stable secondary carbocation Rationalised 2023-24 312 chemistry Anti Markovnikov addition or peroxide effect or Kharash effect In the presence of peroxide, addition of HBr to unsymmetrical alkenes like propene takes place contrary to the Markovnikov rule. This happens only with HBr but not with HCl and HI. This addition reaction was observed by M.S. Kharash and F.R. Mayo in 1933 at the University of Chicago. This reaction is known as peroxide or Kharash effect or addition reaction anti to Markovnikov rule. CH3 – CH=CH2+HBr (C6H5CO)2O2 CH3–CH2 CH2Br 1–Bromopropane (9.43) Mechanism : Peroxide effect proceeds via free radical chain mechanism as given below: (ii) C . 6H5+H–Br Homolysis C6H3+ B. r The secondary free radical obtained in the above mechanism (step iii) is more stable than the primary. This explains the formation of 1-bromopropane as the major product. It may be noted that the peroxide effect is not observed in addition of HCl and HI. This may be due to the fact that the H–Cl bond being stronger (430.5 kJ mol–1) than H–Br bond (363.7 kJ mol–1), is not cleaved by the free radical, whereas the H–I bond is weaker (296.8 kJ mol–1) and iodine free radicals combine to form iodine molecules instead of adding to the double bond. Problem 9.12 Write IUPAC names of the products obtained by addition reactions of HBr to hex-1-ene (i) in the absence of peroxide and (ii) in the presence of peroxide. Solution 4. Addition of sulphuric acid : Cold concentrated sulphuric acid adds to alkenes in accordance with Markovnikov rule to form alkyl hydrogen sulphate by the electrophilic addition reaction. (i) Rationalised 2023-24 Hydrocarbons 313 (9.44) (9.45) 5. Addition of water : In the presence of a few drops of concentrated sulphuric acid alkenes react with water to form alcohols, in accordance with the Markovnikov rule. (9.46) 6. Oxidation: Alkenes on reaction with cold, dilute, aqueous solution of potassium permanganate (Baeyer's reagent) produce vicinal glycols. Decolorisation of KMnO4 solution is used as a test for unsaturation. (9.47) (9.48) b) Acidic potassium permanganate or acidic potassium dichromate oxidises alkenes to ketones and/or acids depending upon the nature of the alkene and the experimental conditions (9.49) CH3 – CH=CH–CH3 KMnO4/H+ 2CH3COOH But-2-ene Ethanoic acid (9.50) 7. Ozonolysis : Ozonolysis of alkenes involves the addition of ozone molecule to alkene to form ozonide, and then cleavage of the ozonide by Zn-H2O to smaller molecules. This reaction is highly useful in detecting the position of the double bond in alkenes or other unsaturated compounds. (9.51) (9.52) 8. Polymerisation: You are familiar with polythene bags and polythene sheets. Polythene is obtained by the combination of large number of ethene molecules at high temperature, high pressure and in the presence of a catalyst. The large molecules thus obtained are called polymers. This reaction is known as polymerisation. The simple compounds from which polymers are made are called Rationalised 2023-24 314 chemistry monomers. Other alkenes also undergo polymerisation. n(CH2 =CH2) High temp./pressure Catalyst —( CH2–CH2 )— Polythene (9.53) n(CH3 –CH=CH2) High temp./pressure Catalyst —( CH–CH2 )—n CH3 Polypropene (9.54) Polymers are used for the manufacture of plastic bags, squeeze bottles, refrigerator dishes, toys, pipes, radio and T.V. cabinets etc. Polypropene is used for the manufacture of milk crates, plastic buckets and other moulded articles. Though these materials have now become common, excessive use of polythene and polypropylene is a matter of great concern for all of us. 9.4 Alkynes Like alkenes, alkynes are also

unsaturated hydrocarbons. They contain at least one triple bond between two carbon atoms. The number of hydrogen atoms is still less in alkynes as compared to alkenes or alkanes. Their general formula is $C_nH_{2n-2}$. The first stable member of alkyne series is ethyne which is popularly known as acetylene. Acetylene is used for arc welding purposes in the form of oxyacetylene flame obtained by mixing acetylene with oxygen gas. Alkynes are starting materials for a large number of organic compounds. Hence, it is interesting to study this class of organic compounds. 9.4.1 Nomenclature and Isomerism In common system, alkynes are named as derivatives of acetylene. In IUPAC system, they are named as derivatives of the corresponding alkanes replacing 'ane' by the suffix 'yne'. The position of the triple bond is indicated by the first triply bonded carbon. Common and IUPAC names of a few members of alkyne series are given in Table 9.2. You have already learnt that ethyne and propyne have got only one structure but there are two possible structures for butyne – (i) but-1-yne and (ii) but-2-yne. Since these two compounds differ in their structures due to the position of the triple bond, they are known as position isomers. In how many ways, you can construct the structure for the next homologue i.e., the next alkyne with molecular formula $C_5H_8$? Let us try to arrange five carbon atoms with a continuous chain and with a side chain. Following are the possible structures : Structure IUPAC name I. 1 2 3 4 5 HC≡ C– CH2– CH2– CH3 Pent–1-yne II. 1 2 3 4 5 H3C–C≡ C– CH2– CH3 Pent–2-yne III. 4 3 2 1 H3C–CH–C≡ CH | CH3 3-Methyl but–1-yne Structures I and II are position isomers and structures I and III or II and III are chain isomers. Problem 9.13 Write structures of different isomers corresponding to the 5th member of alkyne series. Also write IUPAC names of all the isomers. What type of isomerism is exhibited by different pairs of isomers? Solution 5th member of alkyne has the molecular formula $C_6H_{10}$. The possible isomers are: Table 9.2 Common and IUPAC Names of Alkynes ($C_nH_{2n-2}$) Value of n Formula Structure Common name IUPAC name 2 C2H2 H-C≡CH Acetylene Ethyne 3 C3H4 CH3-C≡CH Methylacetylene Propyne 4 C4H6 CH3CH2-C≡CH Ethylacetylene But-1-yne 4 C4H6 CH3-C≡C-CH3 Dimethylacetylene But-2-yne Rationalised 2023-24 Hydrocarbons 315 (a) HC ≡ C – CH2 – CH2 – CH2 – CH3 Hex-1-yne (b) CH3 – C ≡ C – CH2 – CH2 – CH3 Hex-2-yne (c) CH3 – CH2 – C ≡ C – CH2– CH3 Hex-3-yne 3-Methylpent-1-yne 4-Methylpent-1-yne 4-Methylpent-2-yne 3,3-Dimethylbut-1-yne Position and chain isomerism shown by different pairs. 9.4.2 Structure of Triple Bond Ethyne is the simplest molecule of alkyne series. Structure of ethyne is shown in Fig. 9.6. Each carbon atom of ethyne has two sp hybridised orbitals. Carbon-carbon sigma (σ) bond is obtained by the head-on overlapping of the two sp hybridised orbitals of the two carbon atoms. The remaining sp hybridised orbital of each carbon atom undergoes overlapping along the internuclear axis with the 1s orbital of each of the two hydrogen atoms forming two C-H sigma bonds. H-C-C bond angle is of 180°. Each carbon has two unhybridised p orbitals which are perpendicular to each other as well as to the plane of the C-C sigma bond. The 2p orbitals of one carbon atom are parallel to the 2p orbitals of the other carbon atom, which undergo lateral or sideways overlapping to form two pi (π) bonds between two carbon atoms. Thus ethyne molecule consists of one C–C σ bond, two C–H σ bonds and two C–C π bonds. The strength of C≡C bond (bond enthalpy 823 kJ mol-1) is more than those of C=C bond (bond enthalpy 681 kJ mol–1) and C–C bond (bond enthalpy 348 kJ mol–1). The C≡C bond length is shorter (120 pm) than those of C=C (133 pm) and C–C (154 pm). Electron cloud between two carbon atoms is cylindrically symmetrical about the internuclear axis. Thus, ethyne is a linear molecule. 9.4.3 Preparation 1. From calcium carbide: On industrial scale, ethyne is prepared by treating calcium carbide with water. Calcium carbide is prepared by heating quick lime with coke. Quick lime can be obtained by heating limestone as shown in the following reactions: CaCO3 Δ CaO + O2 (9.55) Fig. 9.6 Orbital picture of ethyne showing (a) sigma overlaps (b) pi overlaps. Rationalised 2023-24 316 chemistry CaO + 3C CaC2 + CO (9.56) Calcium carbide CaC2 + 2H2O Ca(OH)2 + C2H2 (9.57) 2. From vicinal dihalides : Vicinal dihalides on treatment with alcoholic potassium hydroxide undergo dehydrohalogenation. One molecule of hydrogen halide is eliminated to form alkenyl halide which on treatment with sodamide gives alkyne.

9.4.4 Properties Physical properties Physical properties of alkynes follow the same trend of alkenes and alkanes. First three members are gases, the next eight are liquids and the higher ones are solids. All alkynes are colourless. Ethyene has characteristic odour. Other members are odourless. Alkynes are weakly polar in nature. They are lighter than water and immiscible with water but soluble in organic solvents like ethers, carbon tetrachloride and benzene. Their melting point, boiling point and density increase with increase in molar mass. Chemical properties Alkynes show acidic nature, addition reactions and polymerisation reactions as follows : A. Acidic character of alkyne: Sodium metal and sodamide ($NaNH_2$) are strong bases. They react with ethyne to form sodium acetylide with the liberation of dihydrogen gas. These reactions have not been observed in case of ethene and ethane thus indicating that ethyne is acidic in nature in comparison to ethene and ethane. Why is it so ? Has it something to do with their structures and the hybridisation ? You have read that hydrogen atoms in ethyne are attached to the sp hybridised carbon atoms whereas they are attached to $sp^2$ hybridised carbon atoms in ethene and $sp^3$ hybridised carbons in ethane. Due to the maximum percentage of s character (50%), the sp hybridised orbitals of carbon atoms in ethyne molecules have highest electronegativity; hence, these attract the shared electron pair of the C-H bond of ethyne to a greater extent than that of the $sp^2$ hybridised orbitals of carbon in ethene and the $sp^3$ hybridised orbital of carbon in ethane. Thus in ethyne, hydrogen atoms can be liberated as protons more easily as compared to ethene and ethane. Hence, hydrogen atoms of ethyne attached to triply bonded carbon atom are acidic in nature. You may note that the hydrogen atoms attached to the triply bonded carbons are acidic but not all the hydrogen atoms of alkynes. $HC \equiv CH + Na \rightarrow HC \equiv C- Na^+ + 1/2 H_2$ Monosodium ethynide (9.59) $HC \equiv C- Na + Na \rightarrow Na^+ C- Na^+ \equiv C- Na^+ + 1/2 H_2$ Disodium ethynide (9.60) $CH_3 - C \equiv C - H + Na^+ NH^-_2 \downarrow CH_3 - C \equiv C- Na^+ + NH_3$ Sodium propynide (9.61) These reactions are not shown by alkenes and alkanes, hence used for distinction between alkynes, alkenes and alkanes. What about the above reactions with but-1-yne and but-2-yne ? Alkanes, alkenes and alkynes follow the following trend in their acidic behaviour : i) $CH \equiv CH > H_2C -CH_2 > CH_3 -CH_3$ ii) $HC \equiv CH > CH_3 -C \equiv CH >> CH_3 -C \equiv C-CH_3$ B. Addition reactions: Alkynes contain a triple bond, so they add up, two molecules of dihydrogen, halogen, hydrogen halides etc. Formation of the addition product takes place according to the following steps. Rationalised 2023-24 Hydrocarbons 317 The addition product formed depends upon stability of vinylic cation. Addition in unsymmetrical alkynes takes place according to Markovnikov rule. Majority of the reactions of alkynes are the examples of electrophilic addition reactions. A few addition reactions are given below: (i) Addition of dihydrogen $HC \equiv CH + H_2$ Pt/Pd/Ni $[H_2C = CH_2]$ $H_2$ $CH_3 - CH_3$ (9.62) $CH_3 - C \equiv CH + H_2$ Pt/Pd/Ni $[CH_3 - CH = CH_2]$ Propyne Propene $\downarrow H_2$ $CH_3 - CH_2 - CH_3$ Propane (9.63) (ii) Addition of halogens (9.64) Reddish orange colour of the solution of bromine in carbon tetrachloride is decolourised. This is used as a test for unsaturation. (iii) Addition of hydrogen halides Two molecules of hydrogen halides (HCl, HBr, HI) add to alkynes to form gem dihalides (in which two halogens are attached to the same carbon atom) $H-C \equiv C-H + H-Br$ $[CH_2 = CH-Br] \rightarrow CHBr_2$ Bromoethene $CH_3$ 1,1-Dibromoethane (9.65) (9.66) (iv) Addition of water Like alkanes and alkenes, alkynes are also immiscible and do not react with water. However, one molecule of water adds to alkynes on warming with mercuric sulphate and dilute sulphuric acid at 333 K to form carbonyl compounds. (9.67) (9.68) (v) Polymerisation (a) Linear polymerisation: Under suitable conditions, linear polymerisation of ethyne takes place to produce polyacetylene or polyethyne which is a high molecular weight polyene containing repeating units of (CH = CH – CH = CH ) and can be represented as —(CH = CH – CH = CH)n— Under special conditions, this polymer conducts electricity. Rationalised 2023-24 318 chemistry Thin film of polyacetylene can be used as electrodes in batteries. These films are good conductors, lighter and cheaper than the metal conductors. (b) Cyclic polymerisation: Ethyne on passing through red hot iron tube at 873K undergoes cyclic polymerization. Three molecules polymerise to form benzene, which is the starting molecule for the preparation of derivatives of benzene, dyes, drugs and large number of other

organic compounds. This is the best route for entering from aliphatic to aromatic compounds as discussed below: (9.69) Problem 9.14 How will you convert ethanoic acid into benzene? Solution 9.5 Aromatic Hydrocarbon These hydrocarbons are also known as 'arenes'. Since most of them possess pleasant odour (Greek; aroma meaning pleasant smelling), the class of compounds was named as 'aromatic compounds'. Most of such compounds were found to contain benzene ring. Benzene ring is highly unsaturated but in a majority of reactions of aromatic compounds, the unsaturation of benzene ring is retained. However, there are examples of aromatic hydrocarbons which do not contain a benzene ring but instead contain other highly unsaturated ring. Aromatic compounds containing benzene ring are known as benzenoids and those not containing a benzene ring are known as non-benzenoids. Some examples of arenes are given below: Benzene Toluene Naphthalene Biphenyl 9.5.1 Nomenclature and Isomerism The nomenclature and isomerism of aromatic hydrocarbons has already been discussed in Unit 8. All six hydrogen atoms in benzene are equivalent; so it forms one and only one type of monosubstituted product. When two hydrogen atoms in benzene are replaced by two similar or different monovalent atoms or groups, three different position isomers are possible. The 1, 2 or 1, 6 is known as the ortho (o–), the 1, 3 or 1, 5 as meta (m–) and the 1, 4 as para (p–) disubstituted compounds. A few examples of derivatives of benzene are given below: Methylbenzene 1,2-Dimethylbenzene (Toluene) (o-Xylene) Rationalised 2023-24 Hydrocarbons 319 1,3 Dimethylbenzene 1,4-Dimethylbenzene (m-Xylene) ( p-Xylene) 9.5.2 Structure of Benzene Benzene was isolated by Michael Faraday in 1825. The molecular formula of benzene, $C_6H_6$, indicates a high degree of unsaturation. This molecular formula did not account for its relationship to corresponding alkanes, alkenes and alkynes which you have studied in earlier sections of this unit. What do you think about its possible structure? Due to its unique properties and unusual stability, it took several years to assign its structure. Benzene was found to be a stable molecule and found to form a triozonide which indicates the presence of three double bonds. Benzene was further found to produce one and only one monosubstituted derivative which indicated that all the six carbon and six hydrogen atoms of benzene are identical. On the basis of this observation August Kekulé in 1865 proposed the following structure for benzene having cyclic arrangement of six carbon atoms with alternate single and double bonds and one hydrogen atom attached to each carbon atom. The Kekulé structure indicates t h e p o s s i b i l i t y o f t w o i s o m e r i c 1, 2-dibromobenzenes. In one of the isomers, the bromine atoms are attached to the doubly bonded carbon atoms whereas in the other, they are attached to the singly bonded carbons. Friedrich August Kekulé,a German chemist was born in 1829 at Darmsdt in Germany. He became Professor in 1856 and Fellow of Royal Society in 1875. He made major contribution to structural organic chemistry by proposing in 1858 that carbon atoms can join to one another to form chains and later in 1865,he found an answer to the challenging problem of benzene structure by suggesting that these chains can close to form rings. He gave the dynamic structural formula to benzene which forms the basis for its modern electronic structure. He described the discovery of benzene structure later as: "I was sitting writing at my textbook,but the work did not progress; my thoughts were elsewhere. I turned my chair to the fire, and dozed. Again the atoms were gambolling before my eyes. This time the smaller groups kept modestly in the background. My mental eye, rendered more acute by repeated visions of this kind, could now distinguish larger structures of manifold conformations; long rows,sometimes more closely fitted together; all twisting and turning in snake like motion. But look! What was that? One of the snakes had seized hold of it's own tail, and the form whirled mockingly before my eyes. As if by a flash of lightning I woke;.... I spent the rest of the night working out the consequences of the hypothesis. Let us learn to dream, gentlemen, and then perhaps we shall learn the truth but let us beware of making our dreams public before they have been approved by the waking mind."( 1890). One hundred years later, on the occasion of Kekulé's centenary celebrations a group of compounds having polybenzenoid structures have been named as Kekulenes. FRIEDRICH

However, benzene was found to form only one ortho disubstituted product. This problem was overcome by Kekulé by suggesting the concept of oscillating nature of double bonds in benzene as given below. Even with this modification, Kekulé structure of benzene fails to explain unusual stability and preference to substitution reactions than addition reactions, which could later on be explained by resonance. Resonance and stability of benzene According to Valence Bond Theory, the concept of oscillating double bonds in benzene is now explained by resonance. Benzene is a hybrid of various resonating structures. The two structures, A and B given by Kekulé are the main contributing structures. The hybrid structure is represented by inserting a circle or a dotted circle in the hexagon as shown in (C). The circle represents the six electrons which are delocalised between the six carbon atoms of the benzene ring. (A) (B) (C) The orbital overlapping gives us better picture about the structure of benzene. All the six carbon atoms in benzene are sp 2 hybridized. Two sp 2 hybrid orbitals of each carbon atom overlap with sp 2 hybrid orbitals of adjacent carbon atoms to form six C—C sigma bonds which are in the hexagonal plane. The remaining sp 2 hybrid orbital of each carbon atom overlaps with s orbital of a hydrogen atom to form six C—H sigma bonds. Each carbon atom is now left with one unhybridised p orbital perpendicular to the plane of the ring as shown below: The unhybridised p orbital of carbon atoms are close enough to form a π bond by lateral overlap. There are two equal possibilities of forming three π bonds by overlap of p orbitals of C1 –C2, C3 – C4, C5 – C6 or C2 – C3, C4 – C5, C6 – C1 respectively as shown in the following figures. Fig. 9.7 (a) Fig. 9.7 (b) Structures shown in Fig. 9.7(a) and (b) correspond to two Kekulé's structure with localised π bonds. The internuclear distance between all the carbon atoms in the ring has been determined by the X-ray diffraction to be the same; there is equal probability for the p orbital of each carbon atom to overlap with the p orbitals of adjacent carbon atoms [Fig. 9.7 (c)]. This can be represented in the form of two doughtnuts (rings) of electron clouds [Fig. 9.7 (d)], one above and one below the plane of the hexagonal ring as shown below: Fig. 9.7 (c) Fig. 9.7 (d) The six π electrons are thus delocalised and can move freely about the six carbon nuclei, instead of any two as shown in Fig. 9.6 (a) or (b). The delocalised π electron cloud is attracted more strongly by the nuclei of the carbon atoms than the electron cloud localised between two carbon atoms. Therefore, presence of delocalised π electrons in benzene makes it more stable than the hypothetical cyclohexatriene. X-Ray diffraction data reveals that benzene is a planar molecule. Had any one of the above structures of benzene (A or B) been correct, two types of C—C bond lengths were expected. However, X-ray data indicates that all the six C—C bond lengths are of the same order (139 pm) which is intermediate between C— C single bond (154 pm) and C—C double bond (133 pm). Thus the absence of pure double bond in benzene accounts for the reluctance of benzene to show addition reactions under normal conditions, thus explaining the unusual behaviour of benzene. 9.5.3 Aromaticity Benzene was considered as parent 'aromatic' compound. Now, the name is applied to all the ring systems whether or not having benzene ring, possessing following characteristics. (i) Planarity (ii) Complete delocalisation of the π electrons in the ring (iii) Presence of (4n + 2) π electrons in the ring where n is an integer (n = 0, 1, 2, . . .). This is often referred to as Hückel Rule. Some examples of aromatic compounds are given below: 9.5.4 Preparation of Benzene Benzene is commercially isolated from coal tar. However, it may be prepared in the laboratory by the following methods. (i) Cyclic polymerisation of ethyne: (Section 9.4.4) (ii) Decarboxylation of aromatic acids: Sodium salt of benzoic acid on heating with sodalime gives benzene. (9.70) (electron cloud) (iii) Reduction of phenol: Phenol is reduced to benzene by passing its vapours over heated zinc dust (9.71) 9.5.5 Properties Physical properties Aromatic hydrocarbons are non- polar molecules and are usually colourless liquids or solids with a characteristic aroma. You are also familiar with naphthalene balls which are used in toilets and for preservation of clothes because of unique smell of the compound and the moth repellent property.

Aromatic hydrocarbons are immiscible with water but are readily miscible with organic solvents. They burn with sooty flame. Chemical properties Arenes are characterised by electrophilic substitution reactions. However, under special conditions they can also undergo addition and oxidation reactions. Electrophilic substitution reactions The common electrophilic substitution reactions of arenes are nitration, halogenation, sulphonation, Friedel Craft's alkylation and acylation reactions in which attacking reagent is an electrophile (E+ ) (i) Nitration: A nitro group is introduced into benzene ring when benzene is heated with a mixture of concentrated nitric acid and concentrated sulphuric acid (nitrating mixture). (9.72) Nitrobenzene (ii) Halogenation: Arenes react with halogens in the presence of a Lewis acid like anhydrous $FeCl_3$, $FeBr_3$ or $AlCl_3$ to yield haloarenes. Chlorobenzene (9.73) (iii) Sulphonation: The replacement of a hydrogen atom by a sulphonic acid group in a ring is called sulphonation. It is carried out by heating benzene with fuming sulphuric acid (oleum). (9.74) (iv) Friedel-Crafts alkylation reaction: When benzene is treated with an alkyl halide in the presence of anhydrous aluminium chloride, alkylbenene is formed. (9.75) (9.76) Why do we get isopropyl benzene on treating benzene with 1-chloropropane instead of n-propyl benzene? (v) Friedel-Crafts acylation reaction: The reaction of benzene with an acyl halide or acid anhydride in the presence of Lewis acids ($AlCl_3$) yields acyl benzene. Rationalised 2023-24 Hydrocarbons 323 (9.77) (9.78) If excess of electrophilic reagent is used, further substitution reaction may take place in which other hydrogen atoms of benzene ring may also be successively replaced by the electrophile. For example, benzene on treatment with excess of chlorine in the presence of anhydrous $AlCl_3$ can be chlorinated to hexachlorobenzene ($C_6Cl_6$) (9.79) Mechanism of electrophilic substitution reactions: According to experimental evidences, SE (S = substitution; E = electrophilic) reactions are supposed to proceed via the following three steps: (a) Generation of the eletrophile (b) Formation of carbocation intermediate (c) Removal of proton from the carbocation intermediate (a) Generation of electrophile $E\oplus$ : During chlorination, alkylation and acylation of benzene, anhydrous $AlCl_3$, being a Lewis acid helps in generation of the elctrophile $Cl\oplus$ , $R\oplus$ , $RC\oplus O$ (acylium ion) respectively by combining with the attacking reagent. In the case of nitration, the electrophile, nitronium ion, is produced by transfer of a proton (from sulphuric acid) to nitric acid in the following manner: Step I Step II Protonated Nitronium nitric acid ion It is interesting to note that in the process of generation of nitronium ion, sulphuric acid serves as an acid and nitric acid as a base. Thus, it is a simple acid-base equilibrium. (b) F o r m a t i o n o f C a r b o c a t i o n (arenium ion): Attack of electrophile results in the formation of σ-complex or arenium ion in which one of the carbon is sp 3 hybridised. sigma complex (arenium ion) The arenium ion gets stabilised by resonance: Rationalised 2023-24 324 chemistry Sigma complex or arenium ion loses its aromatic character because delocalisation of electrons stops at sp 3 hybridised carbon. (c) Removal of proton: To restore the aromatic character, σ -complex releases proton from sp 3 hybridised carbon on attack by [$AlCl_4$] – (in case of halogenation, alkylation and acylation) and [$HSO_4$] – (in case of nitration). Addition reactions Under vigorous conditions, i.e., at high temperature and/ or pressure in the presence of nickel catalyst, hydrogenation of benzene gives cyclohexane. Cyclohexane (9.80) Under ultra-violet light, three chlorine molecules add to benzene to produce benzene hexachloride, $C_6H_6Cl_6$ which is also called gammaxane. Benzene hexachloride, (BHC) (9.81) Combustion: When heated in air, benzene burns with sooty flame producing $CO_2$ and $H_2O$ 6 2 22 6 15 CH O 2 + → 6CO +3H O (9.82) General combustion reaction for any hydrocarbon may be given by the following chemical equation: $C_xH_y$ + (x + ) $O_2$ → x $CO_2$ + $H_2O$ n (9.83) 9.5.6 Directive influence of a functional group in monosubstituted benzene When monosubstituted benzene is subjected to further substitution, three possible disubstituted products are not formed in equal amounts. Two types of behaviour are observed. Either ortho and para products or meta product is predominantly formed. It has also been observed that this behaviour depends on the nature of the substituent already present in the benzene ring and not on the nature of the entering group. This is known as directive influence of substituents. Reasons

for ortho/para or meta directive nature of groups are discussed below: Ortho and para directing groups: The groups which direct the incoming group to ortho and para positions are called ortho and para directing groups. As an example, let us discuss the directive influence of phenolic (–OH) group. Phenol is resonance hybrid of following structures: It is clear from the above resonating structures that the electron density is more on o – and p – positions. Hence, the substitution takes place mainly at these positions. However, it may be noted that –I effect of – OH group also operates due to which the electron density on ortho and para positions of the benzene ring is slightly reduced. But the overall electron density increases at these positions of the ring due to resonance. Therefore, –OH group activates the benzene ring for the attack by Rationalised 2023-24 Hydrocarbons 325 an electrophile. Other examples of activating groups are –NH2, –NHR, –NHCOCH3, –OCH3, –CH3, –C2H5, etc. In the case of aryl halides, halogens are moderately deactivating. Because of their strong –I effect, overall electron density on benzene ring decreases. It makes further substitution difficult. However, due to resonance the electron density on o– and p– positions is greater than that at the m-position. Hence, they are also o – and p – directing groups. Resonance structures of chlorobenzene are given below: In this case, the overall electron density on benzene ring decreases making further substitution difficult, therefore these groups are also called 'deactivating groups'. The electron density on o – and p – position is comparatively less than that at meta position. Hence, the electrophile attacks on comparatively electron rich meta position resulting in meta substitution. 9.6 Carcinogenicity and Toxicity Benzene and polynuclear hydrocarbons containing more than two benzene rings fused together are toxic and said to possess cancer producing (carcinogenic) property. Such polynuclear hydrocarbons are formed on incomplete combustion of organic materials like tobacco, coal and petroleum. They enter into human body and undergo various biochemical reactions and finally damage DNA and cause cancer. Some of the carcinogenic hydrocarbons are given below (see box). Meta directing group: The groups which direct the incoming group to meta position are called meta directing groups. Some examples of meta directing groups are –NO2, –CN, –CHO, –COR, –COOH, –COOR, –SO3H, etc. Let us take the example of nitro group. Nitro group reduces the electron density in the benzene ring due to its strong–I effect. Nitrobenzene is a resonance hybrid of the following structures. Rationalised 2023-24 326 chemistry SUMMARY Hydrocarbons are the compounds of carbon and hydrogen only. Hydrocarbons are mainly obtained from coal and petroleum, which are the major sources of energy. Petrochemicals are the prominent starting materials used for the manufacture of a large number of commercially important products. LPG (liquefied petroleum gas) and CNG (compressed natural gas), the main sources of energy for domestic fuels and the automobile industry, are obtained from petroleum. Hydrocarbons are classified as open chain saturated (alkanes) and unsaturated (alkenes and alkynes), cyclic (alicyclic) and aromatic, according to their structure. The important reactions of alkanes are free radical substitution, combustion, oxidation and aromatization. Alkenes and alkynes undergo addition reactions, which are mainly electrophilic additions. Aromatic hydrocarbons, despite having unsaturation, undergo mainly electrophilic substitution reactions. These undergo addition reactions only under special conditions. Alkanes show conformational isomerism due to free rotation along the C–C sigma bonds. Out of staggered and the eclipsed conformations of ethane, staggered conformation is more stable as hydrogen atoms are farthest apart. Alkenes exhibit geometrical (cis-trans) isomerism due to restricted rotation around the carbon–carbon double bond. Benzene and benzenoid compounds show aromatic character. Aromaticity, the property of being aromatic is possessed by compounds having specific electronic structure characterised by Hückel $(4n+2)\pi$ electron rule. The nature of groups or substituents attached to benzene ring is responsible for activation or deactivation of the benzene ring towards further electrophilic substitution and also for orientation of the incoming group. Some of the polynuclear hydrocarbons having fused benzene ring system have carcinogenic property. EXERCISES 9.1 How do you account for the formation of ethane

during chlorination of methane ? 9.2 Write IUPAC names of the following compounds : (a) $CH_3CH=C(CH_3)_2$ (b) $CH_2=CH-C≡C-CH_3$ (c) (d) $–CH_2–CH_2–CH=CH_2$ (e) (f) $CH_3(CH_2)_4 CH (CH_2)_3 CH_3$ $CH_2 –CH (CH_3)_2$ (g) $CH_3 – CH = CH – CH_2 – CH = CH – CH – CH_2 – CH = CH_2 | C_2H_5$ 9.3 For the following compounds, write structural formulas and IUPAC names for all possible isomers having the number of double or triple bond as indicated : (a) $C_4H_8$ (one double bond) (b) $C_5H_8$ (one triple bond) 9.4 Write IUPAC names of the products obtained by the ozonolysis of the following compounds : (i) Pent-2-ene (ii) 3,4-Dimethylhept-3-ene (iii) 2-Ethylbut-1-ene (iv) 1-Phenylbut-1-ene Rationalised 2023-24 Hydrocarbons 327 9.5 An alkene 'A' on ozonolysis gives a mixture of ethanal and pentan-3-one. Write structure and IUPAC name of 'A'. 9.6 An alkene 'A' contains three C – C, eight C – H σ bonds and one C – C π bond. 'A' on ozonolysis gives two moles of an aldehyde of molar mass 44 u. Write IUPAC name of 'A'. 9.7 Propanal and pentan-3-one are the ozonolysis products of an alkene? What is the structural formula of the alkene? 9.8 Write chemical equations for combustion reaction of the following hydrocarbons: (i) Butane (ii) Pentene (iii) Hexyne (iv) Toluene 9.9 Draw the cis and trans structures of hex-2-ene. Which isomer will have higher b.p. and why? 9.10 Why is benzene extra ordinarily stable though it contains three double bonds? 9.11 What are the necessary conditions for any system to be aromatic? 9.12 Explain why the following systems are not aromatic? (i) (ii) (iii) 9.13 How will you convert benzene into (i) p-nitrobromobenzene (ii) m- nitrochlorobenzene (iii) p - nitrotoluene (iv) acetophenone? 9.14 In the alkane $H_3C – CH_2 – C(CH_3)_2 – CH_2 – CH(CH_3)_2$, identify 1°,2°,3° carbon atoms and give the number of H atoms bonded to each one of these. 9.15 What effect does branching of an alkane chain has on its boiling point? 9.16 Addition of HBr to propene yields 2-bromopropane, while in the presence of benzoyl peroxide, the same reaction yields 1-bromopropane. Explain and give mechanism. 9.17 Write down the products of ozonolysis of 1,2-dimethylbenzene (o-xylene). How does the result support Kekulé structure for benzene? 9.18 Arrange benzene, n-hexane and ethyne in decreasing order of acidic behaviour. Also give reason for this behaviour. 9.19 Why does benzene undergo electrophilic substitution reactions easily and nucleophilic substitutions with difficulty? 9.20 How would you convert the following compounds into benzene? (i) Ethyne (ii) Ethene (iii) Hexane 9.21 Write structures of all the alkenes which on hydrogenation give 2-methylbutane. 9.22 Arrange the following set of compounds in order of their decreasing relative reactivity with an electrophile, $E^+$ (a) Chlorobenzene, 2,4-dinitrochlorobenzene, p-nitrochlorobenzene (b) Toluene, $p-H_3C – C_6H_4 – NO_2$, $p-O_2N – C_6H_4 – NO_2$. 9.23 Out of benzene, m–dinitrobenzene and toluene which will undergo nitration most easily and why? 9.24 Suggest the name of a Lewis acid other than anhydrous aluminium chloride which can be used during ethylation of benzene. 9.25 Why is Wurtz reaction not preferred for the preparation of alkanes containing odd number of carbon atoms? Illustrate your answer by taking one example. Rationalised 2023-24