Name: _____   Student number: _____
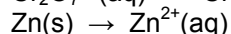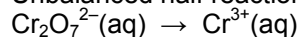
Test 2 2012 Version 1 Solutions

1. Dichromate ions, $Cr_2O_7^{2-}$(aq), react with zinc metal in acid solution to produce Cr^{3+}(aq) and Zn^{2+}(aq) ions. When the reaction is balanced, such that the smallest possible integers appear as stoichiometric coefficients, the coefficient for Zn^{2+} is:
.
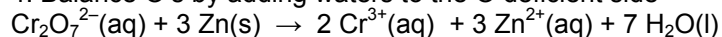A)   2
B)   3
C)   6
D)   1
E)   4

Unbalanced half reactions:
$Cr_2O_7^{2-}$(aq) → Cr^{3+}(aq)
Zn(s) → Zn^{2+}(aq)

1. Balance atoms other than H and O
2. Determine oxidation numbers and include electrons
$Cr_2O_7^{2-}$(aq) + 6 e⁻ → 2 Cr^{3+}(aq)
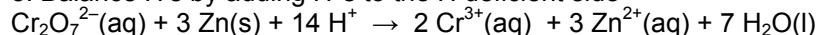Zn(s) → Zn^{2+}(aq) + 2 e⁻
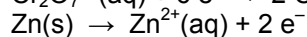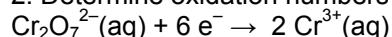
3. Add the half reactions to balance electrons (note that it is easier to balance H's and O's at the end rather than separately for both half reaction – you only have to do it once)
$Cr_2O_7^{2-}$(aq) + 3 Zn(s) → 2 Cr^{3+}(aq) + 3 Zn^{2+}(aq)
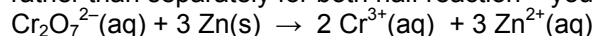
4. Balance O's by adding waters to the O deficient side
$Cr_2O_7^{2-}$(aq) + 3 Zn(s) → 2 Cr^{3+}(aq) + 3 Zn^{2+}(aq) + 7 H_2O(l)

5. Balance H's by adding H⁺s to the H deficient side
$Cr_2O_7^{2-}$(aq) + 3 Zn(s) + 14 H^+ → 2 Cr^{3+}(aq) + 3 Zn^{2+}(aq) + 7 H_2O(l)

Note that steps 4 and 5 are not needed to answer the question, since only the coefficient of Zn^{2+} is required and it is unaffected by the last two steps that balance O's and H's.

2. From the following thermochemical data, what is $\Delta H_f°$**[NO(g)] (in kJ mol⁻¹) ?**
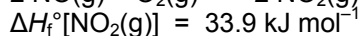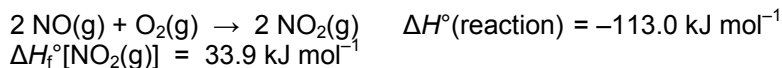
    2 NO(g) + O_2(g) → 2 NO_2(g) $\Delta H°$(reaction) = −113.0 kJ mol⁻¹
    $\Delta H_f°[NO_2(g)]$ = 33.9 kJ mol⁻¹
.
A)   +117.1
B)   +90.4
C)   −90.4
D)   +67.2
E)   −67.3

$\Delta H°$(reaction) = 2 $\Delta H_f°[NO_2(g)]$ − (2 $\Delta H_f°[NO(g)]$ + $\Delta H_f°[O_2(g)]$) = −113.0 kJ mol⁻¹
or (without including units)
2×33.9 − (2 $\Delta H_f°[NO(g)]$ + 0]) = −113.0
So
$\Delta H_f°[NO(g)]$ = 90.4 kJ mol⁻¹

3. Which atom has the **greatest number of *unpaired* electrons** in its ground-state electron configuration?
.

A)   Mn
B)   Ni
C)   N
D)   S
E)   Be

Ground state electron configurations:
Mn: [He] $4s^2\ 3d^5$
Ni: [Ar] $4s^2\ 3d^8$
N: [He] $2s^2\ 2p^3$
S: [Ne] $3s^2\ 3p^4$
Be: [He] $2s^2$

Unpaired electrons occur in unfilled subshells. Thus, we look at the unfilled subshells above and invoke Hund's rule – electrons spread over the orbitals of an unfilled subshell, as much as possible, with electrons having the same spin, as much as possible:

$3d^5$	↑ ↑ ↑ ↑ ↑	5 unpaired electrons	Mn
$3d^8$	↑↓ ↑↓ ↑↓ ↑ ↑	2 unpaired electrons	
$2p^3$	↑ ↑ ↑	3 unpaired electrons	
$3p^4$	↑↓ ↑ ↑	2 unpaired electrons	

4. Dissolving 3.90 g of CaF_2 in 50.0 mL of pure water (density = 1.00 g mL^{-1}) causes the temperature of the water to decrease from 20.00 to 17.32 °C. What is the **molar enthalpy of dissolution** of CaF_2 (in **kJ mol^{-1}**) ? Assume that the specific heat of the solution equals 4.18 J g^{-1} K^{-1} (use the combined mass of water and solute for mass of solution).
.

A)   +10.3
B)   +12.1
C)   −17.6
D)   −12.1
E)   +17.6

q = heat required to return system to its original temperature
  = $C\,\Delta T$ = $m\,s\,\Delta T$ = (3.90 g + 50.0 mL × 1.00 g mL^{-1}) × 4.18 J g^{-1} K^{-1} × (20.00 – 17.32) K
  = 604 J

ΔH = $q\,/\,n$ where n is the number of moles of CaF_2 dissolved.
  = 604 J / (3.90 g / 78.07 g mol^{-1}) = 12100 J mol^{-1} = 12.1 kJ mol^{-1}

5. Calculate the **longest wavelength (in µm)** of light **emitted** by an excited hydrogen atom in which the electron occupies the energy level $n = 6$.
.

A)   93.7
B)   7.46
C)   2.28
D)   1.00
E)   3.28

When an H atom emits light, it drops to a lower n level. The longest wavelength of emitted light corresponds to the smallest frequency which corresponds to the smallest energy difference.
From $n = 6$, the smallest energy difference for an emission process is for $n = 6$ to $n = 5$. Thus,

$\Delta E = (-R_H / 6^2) - (-R_H / 5^2) = R_H (1/ 5^2 - 1/ 6^2) = 2.178 \times 10^{-18} (1/ 25 - 1/ 36)$
$\quad = 2.662 \times 10^{-20}$ J

$\lambda = c / v = h c / \Delta E = 6.6256 \times 10^{-34}$ J s $\times 2.9979 \times 10^8$ m s^{-1} / 2.662×10^{-20} J
$\quad = 7.462 \times 10^{-6}$ m $= 7.462$ µm

6. A sample weighing 0.6760 g that contains an unknown amount of Ba^{2+} ions was completely dissolved in water and treated with an excess of sodium sulfate, Na_2SO_4. A precipitate of $BaSO_4$ formed which was dried and weighed, yielding 0.4105 g. What is the **mass percentage of barium** in the original sample?
.
A) 27.11
B) 39.46
C) 61.72
D) 53.89
E) 35.73

0.4105 g of $BaSO_4$ precipitate corresponds to 0.4105 g / (233.390 g mol^{-1}) $= 0.001758_9$ mol
This means there was 0.001758_9 mol of Ba^{2+} in the original sample – i.e.
$\quad 0.001758_9$ mol $\times 137.327$ g mol^{-1} $= 0.2415_4$ g of Ba^{2+}
The percentage of the original sample that was Ba^{2+} is
$\quad 100\% \times 0.2415_4$ g / 0.6760 g $= 35.73$

7. Which **ONE** of the following pairs of reagents produces **no visible** change (i.e. no gas evolution, precipitate formation, or color change)?
.
A) $Cl_2(aq) + KBr(aq)$
B) $Na_2CO_3(s) + HCl(aq)$
C) $Cu(s) + HCl(aq)$
D) $KCl(aq) + AgClO_4(aq)$
E) $Zn(s) + HI(aq)$

A) $Cl_2(aq) + 2\ KBr(aq) \rightarrow Br_2(aq) + 2\ KCl(aq)$ Bromine is red-brown, whereas the reactants are colorless.

B) $Na_2CO_3(s) + 2\ HCl(aq) \rightarrow 2\ NaCl(aq) + H_2CO_3(aq)$
$H_2CO_3(aq) \rightarrow H_2O(l) + CO_2(g)$ CO_2 gas evolves – we see gas bubbles.

C) $Cu(s) + HCl(aq) \rightarrow$ no reaction H^+ cannot oxidize Cu – Cu is no sufficiently "active".

D) $KCl(aq) + AgClO_4(aq) \rightarrow KClO_4(aq) + AgCl(s)$ There is a silver chloride precipitate.

E) $Zn(s) + 2\ HI(aq) \rightarrow ZnI_2(aq) + H_2(g)$ H_2 gas evolves – we see gas bubbles.

8. The empirical formula of a compound is CH. At 200 °C, 0.147 g of this compound in the gas phase occupies a volume of 97.2 mL at a pressure of 0.75 atm. What is the **molecular formula** of the compound?
.
   A) C_6H_6
   B) C_7H_7
   C) C_5H_5
   D) C_8H_8
   E) C_2H_2

$n = p V / R T = 0.75$ atm $\times 0.0972$ L $/ (0.08206$ L atm K^{-1} mol$^{-1} \times 473$ K$) = 0.00188$ mol
The molar mass of the compound is therefore
        0.147 g / 0.00188 mol $= 78.3$ g mol^{-1}
The molar mass of the CH unit is 13.019 g mol^{-1}.
        78.3 /13.019 $= 6.01$
The compound must be C_6H_6.

9. Put the following atoms in order of **increasing ionization energy**:
.
   A) B < Be < C < F < Na
   B) Be < B < C < F < Na
   C) Na < Be < C < B < F
   D) Na < B < Be < C < F
   E) F < C < B < Be < Na

Ionization energy increases from right to left and going up in the periodic table. So Na must be the smallest. Be comes before B. However, Be has a filled s subshell and its ionization energy is higher than its neighbor to its right, B.

10. Identify the **FALSE** statement(s):
    (i) Lithium fluoride has a lower melting point than potassium iodide. **FALSE**
    (ii) Magnesium has a larger atomic radius than sodium. **FALSE**
    (iii) For some elements, the 2nd ionization energy ($M^+ \rightarrow M^{2+} + e^-$) is smaller than the 1st ionization energy ($M \rightarrow M^+ + e^-$). **FALSE**
.
    A) iii only
    B) ii, iii
    C) i, ii, iii
    D) i only
    E) i, iii

(i) Lattice energy (the negative binding energy of an ionic solid) increases in magnitude when the ions have larger magnitude of charge or are smaller. Thus, LiF has a larger magnitude of lattice energy than KI. The stronger ionic bonding in LiF gives it a higher melting point. Thus, statement (i) is false.
(ii) Atomic radius decreases from left to right along a period of the periodic table. Thus, Mg is smaller than Na. Statement (ii) is false.
(iii) The second ionization energy is always larger than the first. It is harder to take a second electron away. Its binding is stronger than that of the first electron because there is one less repelling electron in the 1+ ion.

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11. Which **ONE** of the following statements is **FALSE**?
.
A)   B has a larger first ionization energy than Al.
B)   S is a smaller atom than Ge.
C)   Be has a larger first ionization energy than Li.
D)   Ca has a larger atomic radius than K.
E)   The ground state electron configuration of P has 3 unpaired electrons.

A) True. B is above Al in the same group.
B) True. Ge is to the left and below S.
C) True. Be is to the right of Li.
D) False. Ca is to the right of K. Atomic radius decreases to the right.
E) True. The ground state electron configuration of P is [Ne] $3s^2\ 3p^3$
$3p^3$ ↑ ↑ ↑   2 unpaired electrons

12. Which of the following statement(s) is(are) **FALSE**?
(i) Al has a higher first ionization energy than Ga. **TRUE**
(ii) Ne atoms are smaller than O atoms. **TRUE**
(iii) K is more easily ionized than Na. **TRUE**
(iv) HNO_3 is a stronger acid than H_2CO_3. **TRUE**
(v) O^{2-} is smaller than Na^+. **FALSE**
.
A)   iii
B)   iv, v
C)   i, ii
D)   iii, iv
E)   v

(i) Al is above Ga in the same group.
(ii) Ne is to the right of O.
(iii) K is below Na, so it has a lower ionization energy – i.e. it is easier to ionize.
(iv) HNO_3 is a strong acid, whereas H_2CO_3 is a weak acid.
(v) O^{2-} and Na^+ have the same electron configuration (i.e. that of Ne), whereas Na^+ has a higher nuclear charge. Therefore, Na^+ is smaller than O^{2-}.

13. Put the following species in order of **increasing atomic radius**:
.
A)   N < Ne < Al < Si < K
B)   Ne < K < Al < Si < N
C)   K < Al < Si < N < Ne
D)   N < Si < Al < Ne < K
E)   Ne < N < Si < Al < K

The sequence of elements, Ne N Si Al K, involves moves to the left and/or down in the periodic table – i.e. moves that increase atomic radius.

14. Which one of the following **decreases** across a row of the periodic table, from **left to right**?
.
A)   Atomic radius
B)   Magnitude of electron affinity
C)   Electronegativity
D)   Ionization energy
E)   Effective nuclear charge

The other properties increase from left to right.

15. For the species NO^+, NO_2^-, NO_3^-, what is the correct **order of increasing** N-O **bond length**?

   .
   A) $NO_2^- < NO^+ < NO_3^-$
   B) $NO_3^- < NO_2^- < NO^+$
   C) $NO^+ < NO_3^- < NO_2^-$
   D) $NO_3^- < NO^+ < NO_2^-$
   E) $NO^+ < NO_2^- < NO_3^-$

Draw the Lewis structures:

   NO^+ NO_2^- NO_3^-,

   2   3/2   4/3
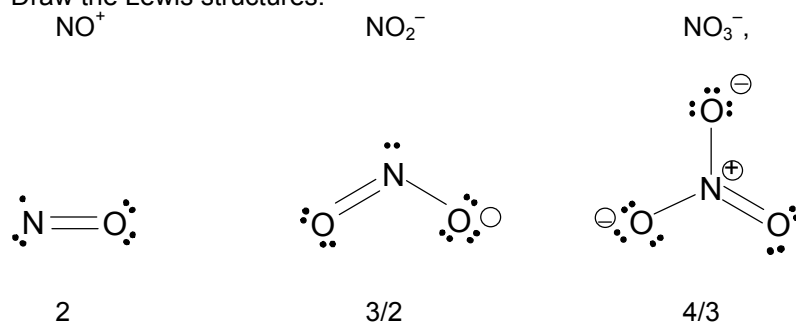
              average NO bond orders

Bond length decreases with increasing bond order.

16. Given $\Delta H_f°[NF_3(g)] = -132$ kJ mol^{-1} and the following bond enthalpy (D) data: $D(N\equiv N) = 946$ kJ mol^{-1}, $D(F–F) = 159$ kJ mol^{-1}, which of the following statements is(are) **FALSE**?

   (i)   The average N–F bond energy in NF_3 is 281 kJ mol^{-1}. **TRUE**
   (ii) $\Delta H_f°[NF_3(g)] > \Delta H_f°[NF_3(l)]$ **TRUE**
   (iii) $\Delta H_f°[F(g)] = 159$ kJ mol^{-1} **FALSE**

   .
   A)   ii
   B)   ii, iii
   C)   i, iii
   D)   iii
   E)   i

(i) $\Delta H_f°[NF_3(g)]$ is the enthalpy of reaction of $1/2\ N_2(g) + 3/2\ F_2(g) \rightarrow NF_3(g)$
This enthalpy of reaction can also be written as
$$1/2\ D(N\equiv N) + 3/2\ D(F–F) - 3\ D(N–F) = \Delta H_f°[NF_3(g)] = -132 \text{ kJ mol}^{-1}$$
$$D(N–F) = 1/3\ (1/2\ D(N\equiv N) + 3/2\ D(F–F) + 132 \text{ kJ mol}^{-1})$$
$$= 1/3\ (1/2 \times 946 + 3/2 \times 159 + 132) \text{ kJ mol}^{-1}$$
$$= 281 \text{ kJ mol}^{-1}$$
(ii) $\Delta H_f°[NF_3(g)] = \Delta H_f°[NF_3(l)] + \Delta H_{vap}°[NF_3] > \Delta H_f°[NF_3(l)]$ because $\Delta H_{vap}°[NF_3] > 0$ (vaporization is always endothermic – intermolecular bonds are broken with no new bonds formed)
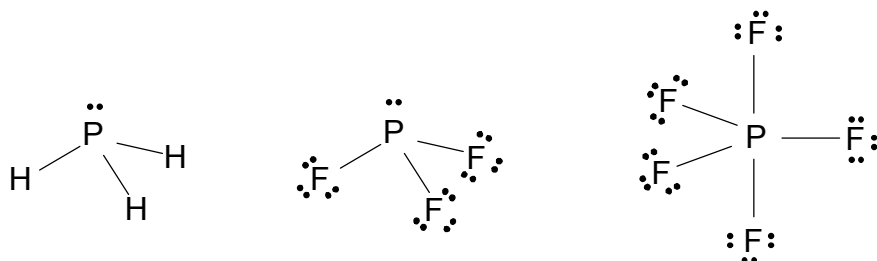
(iii) $\Delta H_f°[F(g)]$ is the enthalpy of reaction of $1/2\ F_2(g) \rightarrow F(g)$
This is ½ $D(F–F) = 159/2$ kJ mol$^{-1} = 79.5$ kJ mol^{-1}

17. Rank the molecules PF_5, PF_3 and PH_3, in order of **increasing molecular dipole moment**?
    (Electronegativity values: P = 2.1; H = 2.2; F = 4.0)
    .
    A) $PF_5 < PF_3 < PH_3$
    B) $PF_3 < PF_5 < PH_3$
    C) $PF_5 < PH_3 < PF_3$
    D) $PH_3 < PF_3 < PF_5$
    E) $PH_3 < PF_5 < PF_3$

Draw the Lewis structures:

PF_5 has no dipole. It has VSEPR class AX_5 and is therefore trigonal bipyramidal. This shape is symmetrical – all bond dipoles cancel out. The remaining two structures are trigonal pyramidal (AX_3E). They are asymmetrical and have net dipole moments. Because the difference in electronegativities is greatest for the P-F bond, PF_3 has the largest dipole moment.

18. Calculate the **lattice enthalpy** (in kJ mol^{-1}) of potassium iodide from the following data:
    ΔH^{o}_f [K(g)] = 89 kJ mol^{-1}
    First ionization energy of K(g) = 418 kJ mol^{-1}
 ΔH^{o}_f [I(g)] = 107 kJ mol^{-1}
    Electron affinity of I = 295 kJ mol^{-1} (NOTE: this number should really be negative- however, the problem was not noticed till after the test went to print)
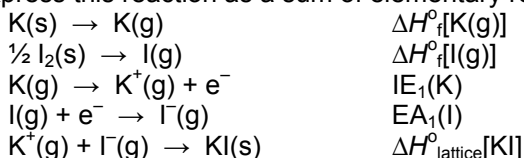 ΔH^{o}_f [KI(s)] = –328 kJ mol^{-1}
    .
    A)   –1237
    B)   –1433
    C)   –681
    D)   –759
    E)   –597

The Born-Haber cycle gives the enthalpy of formation of an ionic solid as a sum of elementary enthalpies.
First, write the formation reaction:
    K(s) + ½ I_2(s) → KI(s) ΔH^{o}_f[KI(s)]
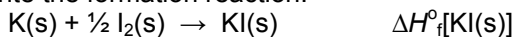
Now express this reaction as a sum of elementary reactions:
    K(s) → K(g) ΔH^{o}_f[K(g)]
    ½ I_2(s) → I(g) ΔH^{o}_f[I(g)]
    K(g) → K^+(g) + e^- IE_1(K)
    I(g) + e^- → I^-(g) EA_1(I)
    K^+(g) + I^-(g) → KI(s) $\Delta H^{o}_{lattice}$[KI]

The enthalpy of formation of KI(s) is the sum of these enthalpies:
    ΔH^{o}_f[KI(s)] = ΔH^{o}_f[K(g)] + ΔH^{o}_f[I(g)] + IE_1(K) + EA_1(I) + $\Delta H^{o}_{lattice}$[KI]

All of the above enthalpies are known, except for the lattice enthalpy. Solve for the lattice enthalpy;
    –328 kJ mol^{-1} = 89 + 107 + 418 + 295 kJ mol^{-1} + $\Delta H^{o}_{lattice}$[KI]

So $\Delta H^o_{lattice}$[KI] = −1237 kJ mol^{-1} (it should really be −647 kJ mol^{-1})

19. Rank the species CO_2, CO, CO_3^{2-} and HCO_2^- in order of **increasing bond enthalpy** of the carbon-oxygen bonds.

   A) CO_3^{2-} < HCO_2^- < CO < CO_2
   B) CO_3^{2-} < HCO_2^- < CO_2 < CO
   C) HCO_2^- < CO_3^{2-} < CO_2 < CO
   D)   CO < CO_2 < HCO_2^- < CO_3^{2-}
   E)   CO < CO_3^{2-} < HCO_2^- < CO_2

Draw the Lewis structures:

   CO_3^{2-} HCO_2^- CO_2 CO

   4/3   3/2   2   3
                                   average CO bond orders
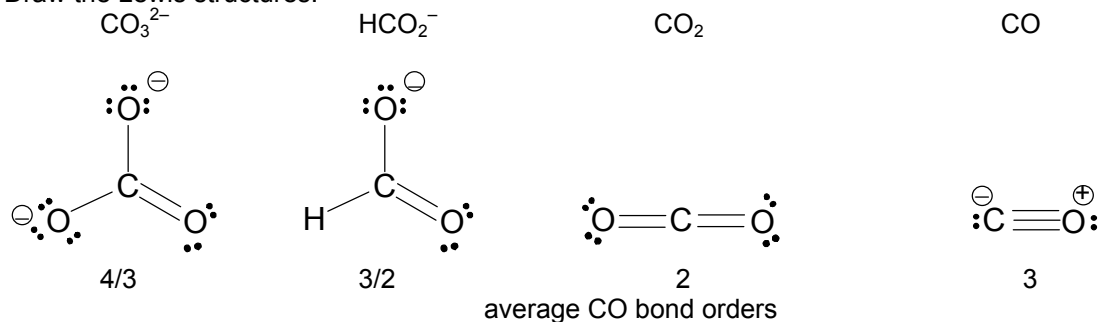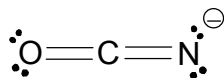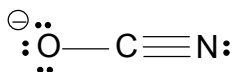
Higher bond order gives higher bond enthalpy.

20. C is the central atom in the thiocyanate anion, OCÑ. The **best** Lewis structure has the following **O, C and N formal charges**, respectively:

   A)   ⁻1, 0, 0
   B)   0, +1, ⁻2
   C)   0, 0, ⁻1
   D)   ⁻1, +1, ⁻1
   E)   ⁻2, +1, 0

The alternative, , places the negative formal charge on N. However, O is more electronegative. So, the first structure is better.

21. Put the following salts in the expected order of increasing magnitude of lattice enthalpy: LiF, KBr, BaS, CaO, $MgCl_2$

   A)   KBr < LiF < $MgCl_2$ < BaS < CaO
   B)   LiF < $MgCl_2$ < CaO < KBr < BaS
   C)   LiF < KBr < $MgCl_2$ < CaO < BaS
   D) $MgCl_2$ < BaS < CaO < LiF < KBr
   E)   KBr < LiF < CaO < BaS < $MgCl_2$

The magnitude of lattice enthalpy depends first on the charge of the ions (higher magnitude of charge means higher magnitude of lattice energy), then on the distance between ions (smaller ions produce higher magnitude lattice energy).

Thus, the salts with the 2+ and 2– ions have the largest magnitude of lattice enthalpy – i.e. BaS and CaO. Since Ca^{2+} ions are smaller than Ba^{2+} ions, and O^{2-} ions are smaller than S^{2-} ions, CaO has a larger magnitude lattice enthalpy than BaS. After that, comes the salt with a 2+ cation and 1– anions; namely, $MgCl_2$. The salts of singly charged ions have the lowest magnitude of lattice enthalpy – LiF is larger because the ions are smaller (Li^+ is smaller than K^+ and F^- is smaller than Br^-).

22. Which one of the following species has an **unpaired electron**?

.
A) ClO
B) ICl_2^+
C) I_3^-
D) NO_2^+
E) ClO_2^-

Draw the Lewis structures:

ClO ICl_2^+ I_3^- NO_2^+ ClO_2^-
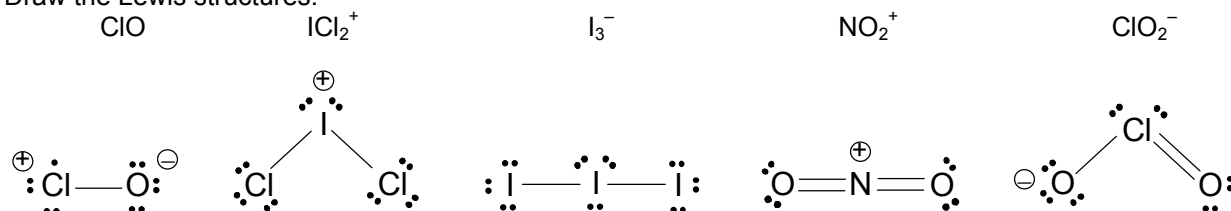

Only ClO has an unpaired electron. We could have predicted this by noted that ClO has an odd number of valence electrons (it has 13 valence electrons), whereas the other species all have an even number of valence electrons (20, 22, 16 and 20, respectively).

23. Which **two** of the following statements are **FALSE**?

(i) ClF_3 is T-shaped.   **TRUE**
(ii)   The chlorine atom in ClF_3 has three nonbonded electrons pairs.   **FALSE**
(iii)   The average bond order in NO_3^- is 4/3.   **TRUE**
(iv) NO_3^- is trigonal pyramidal.   **FALSE**
(v)   The formal charge on N in NO_3^- is +1.   **TRUE**

.
A)   iii, v
B)   iii, iv
C)   i, ii
D)   ii, iv
E)   i, iii

Draw the Lewis structures:

ClF_3 NO_3^-
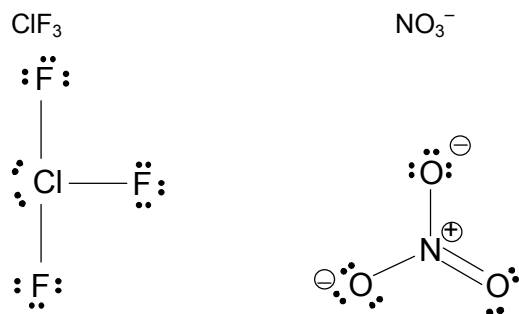
(i) ClF_3 is AX_3E_2 T-shaped

(ii) Cl has 2 nonbonded electron pairs in ClF_3

(iii) & (v) Because N is in period 2, it cannot overfill. This leaves a formal charge of +1 on N, two single bonds and a double bond to O atoms. Average bond order = (1+1+2)/3 = 4/3

(iv) NO_3^- is AX_3 trigonal planar

24. For the heterogeneous reaction: $CaCO_3(s) \rightleftarrows CaO(s) + CO_2(g)$, the equilibrium constant at 112°C is $K = 0.220$. If the partial pressure of $CO_2(g)$ is 0.50 atm at this same temperature, which **one** of the following statements is **TRUE**?
.
   A) $Q < K$, the reaction will proceed to the left.
   B) $Q > K$, the reaction will proceed to the left.
   C) $Q < K$, the reaction will proceed to the right.
   D) $Q = K$, the system is at equilibrium.
   E) $Q > K$, the reaction will proceed to the right.

$Q = p(CO_2)$ the other two species are pure solids with activity = 1 (they do not appear in Q or K)
   $= 0.50 > 0.220$

Therefore, $Q > K$. There will be net reaction shifting Q towards K (i.e. reducing the partial pressure of CO_2) – i.e. there is net reverse reaction (i.e. to the left).

25. Select the **one FALSE** statement concerning the equilibrium $MgCO_3(s) \rightleftarrows MgO(s) + CO_2(g)$ for which $\Delta H° = 100.6$ kJ.
.
   A) Adding MgO(s) does not change the amount of $MgCO_3(s)$.
   B) Halving the size of the reaction vessel increases the amount of $MgCO_3(s)$.
   C) Doubling the amount of all three species (with the volume of the reaction vessel fixed) has no effect on the equilibrium.
   D) Increasing the temperature increases the amount of MgO(s).
   E) Removing $CO_2(g)$ increases the amount of MgO(s).

A) MgO(s) is a pure solid. Adding or removing it does not affect the equilibrium.
B) Halving the size of the reaction vessel doubles the partial pressure of CO_2 (a product). There will be net reverse reaction which increases the amount of $MgCO_3(s)$.
C) Doubling the amount of $MgCO_3(s)$ and MgO(s) has no affect on the equilibrium. However, doubling the amount of $CO_2(g)$ (with fixed volume) doubles its partial pressure, shifting the equilibrium back to reactants.
D) Increasing the temperature favors the endothermic direction (the forward reaction in this case). This increases the amount of product, MgO(s).
E) Removing $CO_2(g)$ (a product) shifts the equilibrium towards products – i.e. increasing the amount of MgO(s).

26. Pure NOBr(g) is introduced in an evacuated container. It dissociates according to the following equilibrium:
$$2\ NOBr(g) \rightleftarrows 2\ NO(g) + Br_2(g)$$
When equilibrium is established at 25 °C, NOBr is 34% dissociated and the total equilibrium pressure P is 0.25 atm. What is K (i.e. K_p) for this equilibrium?
.
   A) 0.0096
   B) 7.8×10^{-6}
   C) 0.016
   D) 0.083
   E) 0.29

Make an I.C.E. table:

In the table, the initial partial pressure of NOBr – p_i – is unknown.

	2 NOBr(g)	⇌	2 NO(g)	+	Br$_2$(g)
Initial	p_i		0		0
Change	$-2x$		$+2x$		$+x$
Equilibrium	$p_i - 2x$		$2x$		x

At equilibrium, we know that NOBr is 34% dissociated. Therefore,

$p_i - 2x = 0.66\,p_i$ (partial pressure is proportional to amount – so equilibrium partial pressure of NOBr is 66% of its initial partial pressure).
Therefore, $0.34\,p_i = 2x$ or $x = 0.17\,p_i$

We also know that the total pressure at equilibrium is 0.25 atm. From the table, the total pressure at equilibrium (the sum of the partial pressures of the three gases) is

$p_i - 2x + 2x + x = p_i + x = 1.17\,p_i = 0.25$ atm

Therefore, $p_i = 0.25$ atm $= 0.21_4$ atm   and $x = 0.036_3$ atm
and the equilibrium constant is

$$K = p(Br_2)\,p^2(NO) / p^2(NOBr) = 4\,x^3 / (p_i - 2x)^2 = 4 \times (0.036_3)^3 / (0.21_4 - 0.072_6)^2 = 0.0096$$

27. A vessel is filled with N$_2$O$_4$(g) to an initial pressure of 3.01 atm. Some of this gas decomposes into NO$_2$(g). At equilibrium, the partial pressure of N$_2$O$_4$(g) is found to be 2.71 atm. What is the value of the equilibrium constant for the decomposition of N$_2$O$_4$(g) into NO$_2$(g), at the temperature of this experiment?
    .
    A)   0.216
    B)   0.133 (it actually said 0.132 on your exam paper)
    C)   1.43
    D)   3.47
    E)   1.59

Make an I.C.E. table:

	N$_2$O$_4$(g)	⇌	2 NO$_2$(g)
Initial	3.01		0
Change	$-x$		$+2x$
Equilibrium	$3.01 - x$		$2x$

At equilibrium, $p(N_2O_4)$ (in atm) $= 3.01 - x = 2.71$.
Therefore, $x = 3.01 - 2.71 = 0.30$ and $p(NO_2) = 0.60$ atm

The equilibrium constant is

$$K = p^2(NO_2) / p(N_2O_4) = 0.60^2 / 2.71 = 0.133$$

28. Given that K_{sp} for CaF_2 is 5.3×10^{-9}, determine the **molar solubility** of CaF_2 in mol L^{-1}.

.
A) 1.7×10^{-4}
B) 0.0011
C) 6.1×10^{-9}
D) 0.021
E) 2.3×10^{-3}

	$CaF_2(s)$	$\rightleftharpoons$	$Ca^{2+}(aq)$	+	$2 F^-(aq)$
Initial			0		0
Change			$+x$		$+2x$
Equilibrium			x		$2x$

K_{sp} = 5.3×10^{-9} = $[Ca^{2+}][F^-]^2$ = $x(2x)^2$ = $4x^3$

Therefore, x = $(K_{sp}/4)^{1/3}$ = $(5.3 \times 10^{-9}/4)^{1/3}$ = 0.0011

This is also the molar solutbilty, $[CaF_2]$ = $[Ca^{2+}]$ = x = 0.0011 mol L^{-1}

29. At 125ºC, K = 0.25 for the decomposition of sodium hydrogen carbonate,
        $2 NaHCO_3(s) \rightleftharpoons Na_2CO_3(s) + CO_2(g) + H_2O(g)$.
   If 10.0 g are added to a 1.00 L flask which is then heated to 125ºC, what is the partial pressure of CO_2 in the flask when the reaction comes to equilibrium?

.
A) 0.75 atm
B) 0.50 atm
C) 1.25 atm
D) 1.0 atm
E) 0.25 atm

	$2 NaHCO_3(s)$	$\rightleftharpoons$	$Na_2CO_3(s)$	+	$CO_2(g)$	+	$H_2O(g)$
Initial					0		0
Change					$+x$		$+x$
Equilibrium					x		x

K = 0.25 = $p(CO_2)\,p(H_2O)$ = x^2

Therefore, x = $(0.25)^{1/2}$ = 0.50 = $p(CO_2)$ at equilibrium (in atm)

30. Which **one** of the following equilibria is **unaffected** when the volume of the reaction vessel is **doubled**?

.
A) $PC1_5(g) \rightleftarrows PCl_3(g) + Cl_2(g)$
B) $2\ SO_2(g) + O_2(g) \rightleftarrows 2\ SO_3(g)$
C) $N_2(g) + O_2(g) \rightleftarrows 2\ NO(g)$
D) $2\ NO_2(g) + 7\ H_2(g) \rightleftarrows 2\ NH_3(g) + 4\ H_2O(l)$
E) $Br_2(g) \rightleftarrows 2\ Br(g)$

Only equilibriums with equal numbers of moles of gas on both sides of the reaction – i.e. $\Delta n_{gas} = 0$ – are unaffected by a change in volume. Doubling the volume causes all partial pressures to change by the factor, ½ . When $\Delta n_{gas} = 0$, the number of partial pressures in the numerator of Q equals the number of partial pressures in the denominator. In this case, the number of ½ factors in the numerator (introduced by the changed volume) equals the number of ½ factors in the denominator. These factors cancel leaving Q unchanged – i.e. it is still equal to K (the system is at equilibrium before the vessel is doubled in size).