

## General and Physical Chemistry.

**A Source of Intense Monochromatic Light.** By CH. FABRY and A. PEROT (*Compt. rend.*, 1899, 128, 1156—1158).—An electric arc is employed passing between mercury poles in a vacuum. The apparatus consists of a cylindrical glass bulb filled to one-third its height with mercury, which is divided into two masses insulated from one another by means of a glass tube concentric with the walls of the bulb and opening nearly on a level with the mercury. Each mass of mercury is connected with a pole of a source of a continuous current by means of platinum wires fused through the glass. The bulb is made as completely vacuum as possible, and in order to strike the arc the apparatus is slightly shaken, which brings the two masses of mercury momentarily in contact. The difference of potential between the poles does not exceed 15 volts, but in order to secure a steady arc, 30 volts should be available. A current of two to three ampères is sufficient, but stronger currents may be used, and the intensity of the light may reach 1 Carcel (approx. 7·4 candles).

The spectrum of the light is identical with that of the light from Michelson's mercury vapour tubes, and consists of a violet ray 4358·0, a green ray 5460·7424, and two yellow rays 5769·5984 and 5790·6593; the separate rays can be isolated by means of a prism or by the use of suitable absorbents, such as yellow glass or potassium dichromate for the violet ray, a saturated solution of didymium chloride for the two yellow rays, and a solution of eosin for the violet and green rays. For photographic purposes, the ultraviolet rays should be cut off by an acid solution of quinine sulphate.

C. H. B.

**Double-trough Refractometer, and Experiments therewith on Solutions of Cadmium Bromide, Sugar, and Di- and Trichloroacetic Acids and their Potassium Salts.** By WILHELM HALLWACHS (*Ann. Phys. Chem.*, 1899, [ii], 68, 1—45).—A form of refractometer is described which consists essentially of a trough of which two opposite sides are formed by two slightly inclined plates of glass with parallel surfaces. This is divided into two by a partition of glass with sides not perfectly parallel. On one side of the partition the trough contains water, and on the other the liquid under examination (*Ann. Phys. Chem.*, 1893, [ii], 50, 577). The incident ray grazes the surface of the partition, passes into it at the critical angle, enters the second liquid, and finally emerges from the trough. The angle between the emergent rays when the incident ray is (1) direct, (2) reversed, is observed, and from this the difference between the refractive indices of the two liquids. The necessary calculations are given and the required expressions deduced, and experiments are recorded to show the accuracy attainable as well as the effect of temperature changes in either or both the trough divisions; differences of 0·0003 in the indices of refraction appear to be measurable with an accuracy of about 0·0000015. Le Blanc and Rohland

(Abstr., 1896, ii, 345) have found that the difference between the molecular refraction of cadmium bromide and iodide, which are but slightly dissociated, varies considerably from that between other more highly dissociated bromides and iodides in solution, but the author's results are not in accord with these, whilst he also shows that the density observations of Le Blanc and Rohland for cadmium bromide do not agree with those of Grotian and Kremers. The error was probably due to the neglect of the hydration of cadmium bromide, as corrections on this assumption bring all the observations into accord, and no indication is given of dependence of refraction on dissociation. For solutions of cane sugar, the change in the refraction is only about 0.4 per cent. between 0.4 and 13 per cent. solutions. A comparison of the differences between the refraction of the acid and its potassium salt in the cases of hydrochloric, dichloroacetic, and trichloroacetic acids shows that at great dilution the differences are very nearly equal—4.6 to 4.9—whereas at higher concentrations the differences are considerably greater, so that in hydrogen salts a connection between refraction and dissociation is indicated, as stated by Le Blanc (*loc. cit.*).  
L. M. J.

**Internal Resistance of Normal Cells.** By ERNST COHEN (*Zeit. physikal. Chem.*, 1899, 28, 723—736).—Measurements of the internal resistance of Clark's and Weston's cells have yielded very diverse values, and the author has investigated the cause of these differences. It was found that the formation of crystals between the electrodes greatly increases the resistance of saturated solutions of zinc sulphate, whilst the resistance is also dependent on the arrangement of the crystals, and this is the cause of the various values found with the normal cells. When filled with a clear saturated solution, the resistance of a Clark's cell at different temperatures was found to be proportional to that of the zinc sulphate solution, and analogous results were obtained with Weston cells. Thus prepared with clear solutions and a small quantity of depolariser, normal cells can be conveniently employed for the graduation of galvanometer readings. L. M. J.

**Relation between the Dissociative Power, the Dielectric Constant, and the Molecular Condition of Liquids.** By HANS EULER (*Zeit. physikal. Chem.*, 1899, 28, 619—628).—According to Dutoit, Aston, and Friderich, the dissociative power of a solvent is a direct function of its molecular association (Abstr., 1897, ii, 546); Nernst has also shown that a probable connection exists between the dissociative power and the dielectric constant (Abstr., 1894, ii, 266). As, however, the associated solvents employed by Aston and Dutoit in all cases had a high dielectric constant, further investigation was necessary. Solutions of potassium iodide and chloride, and of sodium bromide and iodide in nitrobenzene, benzonitrile, and furfuran, were found to have considerable conductivity, and are hence dissociated, although the solvents are in each case non-associated or monomolecular. In the case of the solutions in benzonitrile, the molecular conductivity was found to increase with the concentration, and this is considered to be due to an increased dissociative power owing to the presence of ions; this explanation probably accounts also for some of the exceptions

from the dilution law. The molecular conductivity of the same salts in butyric, isobutyric, and valeric acids was found to be exceedingly small, although the association of the solvents is great. The dielectric constants are, however, also small, and Nernst's hypothesis is hence supported. L. M. J.

**Electric Conductivity of Salt Solutions.** By R. GOLDSCHMIDT and ALBERT REYCHLER (*Bull. Soc. Chim.*, 1898, 19, [iii], 675—684).—An apparatus is described for determining electric conductivity, which is much smaller than the forms employed by Kohlrausch and Arrhenius. The electrolytic cell consists of a small ebonite cup, at the bottom of which is placed a platinum electrode coated with platinum black; the second electrode is fixed to the lower end of a vertical ebonite rod, and both the rod and the cup can be moved to and from each other in a vertical direction by means of micrometer screws. The exact distance between the electrodes is ascertained by means of a vernier and graduated circle attached to the movable parts of the apparatus. In one series of experiments, the diameters of the cup and electrodes were 47 mm. and 40 mm. respectively; a  $N/50$  solution of potassium chloride was employed as the electrolyte, and the temperature of the apparatus was maintained at  $18^\circ$ . The electric capacity of the apparatus was calculated from the equation,  $0.002244 = 1/R \times \text{capacity}$ , the fraction 0.002244 being Kohlrausch's value for the specific conductivity of the solution, the value of the resistance,  $R$ , being determined with the electrodes at varying distances apart. These values were employed in determining the specific conductivity of a  $N/500$  solution of the same electrolyte. The results are arranged in tabular form and compared with those obtained from an apparatus of the Arrhenius form.

A second series of experiments was made with a smaller apparatus, the diameters of the cup and electrodes in this case being 17.3 mm. and 14.3 mm. respectively, and the cup having a capacity of 3 c.c. It is found that the conductivity increases as the distance between the electrodes diminishes. The irregularity observed when the electrodes are very close together is due, not only to polarisation, but also to the abnormal behaviour of the layers of the solution in close proximity to the electrodes. The ratio between the increase of resistance and the increase of the distance between the electrodes is constant only for that portion of the electrolytic solution where the equipotential surfaces are plane and parallel to each other; this condition does not obtain in the immediate neighbourhood of the electrodes. In order to eliminate this source of error, the conductivity of the solution is calculated in the following manner:  $R_m$  and  $R_n$  being the resistances obtained with the standard solution when the electrodes are  $m$  and  $n$  millimetres apart, and  $R'm$  and  $R'n$  the corresponding values for the solution under investigation, the specific conductivity of the latter is  $0.002244 \times (R_m - R_n)/R'm - R'n$ . A table is given which shows that, by the aid of this expression, it is possible to obtain accurate results with the smaller apparatus; in working with this form, it is convenient to fix the key of the Kohlrausch bridge at a convenient resistance, and then to make the final adjustment by

means of the micrometer screw of the upper electrode. The electric capacity of the instrument having been previously determined for any position of the electrodes, the specific conductivity is readily obtained from the equation  $\text{sp. c.} = 1/R' \times \text{capacity}$ . G. T. M.

**Electrical Oscillations.** By HUGO KAUFFMANN (*Zeit. physikal. Chem.*, 1899, 28, 673—707).—Drude has shown that hydroxy-compounds are characterised by anomalous absorption of electrical oscillations (Abstr., 1897, ii, 537). The author, however, shows that this is not limited to such compounds, and considers it to be associated with compounds containing some feeble union. In the series of saturated fatty alcohols, the extent of this absorption does not follow the same order as the velocities of hydrolysis, which may be taken as a measure of the looseness of the hydrogen union in the hydroxyl, and the author therefore considers that the absorption is most marked for a certain "critical stability" and decreases as the stability is removed in either sense from this. Besides hydroxyl, the following groups appear to cause anomalous absorption: nitro-group,  $\text{NO}_2$ ; azoxy-group,  $\text{N}_2\text{O}$ ; the characteristic group,  $:\text{CH}$ , in the leuco-bases, and the carboxyl group in the ethereal salts of substituted carboxylic acids. The absorption of Tesla oscillations by organic compounds in the state of vapour was also further examined (Abstr., 1898, ii, 550), about 75 more compounds being investigated. The following generalisations are now deducible. Aromatic compounds exhibit a much more marked luminescence than aliphatic compounds. Halogens or the nitro-group destroy or weaken the luminescence (this is very marked in naphthalene compounds). Introduction of an acetyl group in a hydroxy-compound or an amine destroys or lowers the luminescence, but the introduction of an alkyl group has no effect. The amido-group converts an inactive into an active compound, whilst two hydroxyl groups produce the same effect, one being, however, insufficient; the author applies the term 'auxochrome' to the groups  $\text{NH}_2$  and  $\text{OH}$  or their derivatives. In di-derivatives of the benzene series, the para-compound is, as a rule, the most active, the cause of the activity probably lies in the nature of the benzene nucleus, and in active compounds there appears to be a predisposition to the formation of compounds of quinonoid structure, although the quinones themselves are inactive. L. M. J.

**Regularities in the Boiling Point of Liquids in Exhausted Vessels.** By FRIEDRICH KRAFFT (*Ber.*, 1899, 32, 1623—1635 Compare Abstr., 1896, ii, 89, 464 and 635).—I. In the distillation of high molecular liquids in the vacuum of the cathode light, the difference in temperature between the liquid and vapour is very slight; thus, palmitic acid, boiling in the vacuum of the cathode rays, showed a temperature of  $137.5$ — $138^\circ$  in the liquid, and  $136$ — $137^\circ$  in the vapour. The boiling point is, however, influenced very largely by the height of the vapour column above the liquid; thus, elaidic acid begins to boil at  $142^\circ$ , but the boiling point rises to  $154^\circ$  as the vapour column mounts up to the side-limb of the distilling flask, 65 mm. above the surface of the liquid. The vapour column is very sharply defined; it

can be measured to 1 mm., and a bright cathode light can be obtained only 20 or 30 mm. above the limit of the saturated vapour.

II. By exact measurement, it was found that phenyl pentadecyl ketone boiled at  $161^{\circ}$  under a vapour column of 90 mm., at  $164.5^{\circ}$  for 110 mm., at  $170.5^{\circ}$  for 145 mm., and at  $176^{\circ}$  for 180 mm., giving an average rise of  $1.66^{\circ}$  in the boiling point for an increase of 10 mm. in the height of the vapour column. An increase in the height of the vapour column from 65 to 180 mm. gave, for lauric acid, mol. wt. 200, a rise in boiling point of  $9.5^{\circ}$ ; for palmitic acid, mol. wt. 256, a rise of  $15.7^{\circ}$ , and for elaidic acid, mol. wt. 282, a rise of  $19^{\circ}$ ; these increments are not proportional to the molecular weights, but the value for palmitic acid is  $6.2^{\circ} = 2 \times 3.1^{\circ}$  greater than that for lauric acid for a difference of 56 in mol. wt., whilst the value for elaidic acid is  $9.5^{\circ} = 3 \times 3.16^{\circ}$  greater for a difference of 82 in mol. wt. The rise of temperature on increasing the height of the vapour column from 65 to 175 mm. was  $18^{\circ}$  for hexadecane, mol. wt. 226, and  $36^{\circ}$  for dotriacontane, mol. wt. 450, so that an exact proportionality appears to exist in the paraffin series.

III. The interval between the melting point and the boiling point of the higher paraffins under 15 mm. pressure increases by  $6^{\circ}$  for each additional  $\text{CH}_2$  group. If, however, the boiling points are determined in a vacuum at 0 mm. pressure, with a vapour column of 65 mm., the regularity is still more marked, for the interval between melting point and boiling point can be calculated directly from the formula  $n \times 4.22^{\circ}$ , where  $n$  is the number of carbon atoms in the molecule; the agreement between the observed and calculated values is very close from  $\text{C}_{20}\text{H}_{42}$  to  $\text{C}_{32}\text{H}_{66}$ , but for the lower homologues the calculated values are always greater than the observed, the deviation being explained by the gradual change in the percentage composition of the paraffin. For the fatty acids, the corresponding increment is about  $4.6^{\circ}$  for each additional  $\text{CH}_2$  group. T. M. L.

[Thermochemistry of] Morphine and its Salts. By ÉMILE LEROY (*Compt. rend.*, 1899, 128, 1107—1110).—The heat of combustion of hydrated morphine is 2146.7 Cal. at constant pressure and 2145.2 Cal. at constant volume. The heat of solution of the anhydrous base is 8.51 Cal., and that of the hydrate is 4.85 Cal.; hence the heats of hydration of morphine with water and ice are 3.66 and 2.10 Cal. respectively. The heat of formation of anhydrous morphine from its elements is 108.24 Cal. The following table gives the heat of neutralisation with various acids.

	Morphine hydrate.	Anhydrous base.
Hydrochloric acid.....	3.52 Cal.	7.18 Cal.
Sulphuric     ,, ( $\frac{1}{2}\text{H}_2\text{SO}_4$ )...	4.85   ,,	8.51   ,,
Nitric         ,, .....	3.39   ,,	7.05   ,,
Acetic         ,, .....	2.70   ,,	6.36   ,,
Oxalic         ,, ( $\frac{1}{2}\text{H}_2\text{C}_2\text{O}_4$ )..	3.66   ,,	7.32   ,,



The addition of excess of acid produces a slight thermic effect, which is positive in the case of the monobasic acids and negative with the dibasic acids; the addition of excess of base is not accompanied by any thermal change.

The heats of solution of the crystalline salts,  $\bar{M}, HCl, 3H_2O$ ,  $M_2, H_2SO_4, 5H_2O$ , and  $M_2, H_2C_2O_4, 4H_2O$ , are  $-9.47$ ,  $-9.74$ , and  $-9.87$  Cal. respectively; the heat of hydration of the hydrochloride with  $3H_2O$  (liquid) is  $6.08$  Cal., and with  $3H_2O$  (solid)  $1.39$  Cal. The heat of formation of the dry hydrochloride from anhydrous morphine and hydrogen chloride is  $27.97$  Cal.; the corresponding constants for isoquinoline and paratoluidine are  $25.67$  and  $23.65$  Cal. respectively; morphine is the stronger base; it is alkaline to litmus, whereas the other two are not. The heat of solution of morphine hydrate in dilute caustic potash at  $12^\circ$  is  $4.79$  Cal.; the heat of formation of the potassium derivative from anhydrous morphine is  $8.45$  Cal., whereas that of potassium phenoxide from solid phenol and dilute potash solution is only  $5.6$  Cal. The addition of a second molecule of morphine or alkali hydroxide produces a development of heat; this result indicates that the potassium derivative is slightly dissociated in aqueous solution. The heat developed by the decomposition of morphine hydrochloride (1 mol.) dissolved in 10 litres of water by caustic potash (1 mol.) is  $10.52$  Cal.; when the precipitated morphine is redissolved by the addition of more potash (1 mol.), the heat generated is  $4.75$  Cal.; this value is almost identical with the heat of solution of crystallised morphine hydrate in caustic potash. The heat effect due to the precipitation of the alkaloid is not produced instantaneously, but during an interval of 2 or 3 minutes; these results indicate that morphine liberated from its salts by an alkali is slowly converted into the hydrated form.

G. T. M.

**Increase of Pressure caused by the Mixture of two Gases, and the Compressibility of the Mixture.** By DANIEL BERTHELOT (*Compt. rend.*, 1899, 128, 1159—1160).—The values calculated for the increase in pressure due to the mixing of gases, assuming a series of operations such that diffusion takes place in a state of perfect gas and using the values for compressibility determined by the author and Sacerdote (this vol., ii, 404), agree closely with the experimental results, and hence the use of the cycle proposed (*loc. cit.*) is justifiable. C. H. B.

**Calculation of the Compressibility of a Gaseous Mixture from that of its Components.** By DANIEL BERTHELOT (*Compt. rend.*, 1899, 128, 1229—1231).—A mathematical discussion not suitable for abstraction.

G. T. M.

**Baumé's Hydrometer—American Standard.** By SIDNEY S. EMERY (*J. Amer. Chem. Soc.*, 1899, 21, 119—132).—Tables are given of the specific gravities corresponding with every  $1/10$  or every  $1/8$  degree of Baumé's scale, from sp. gr.  $0.6667$  to  $1.9833$ . T. M. L.

**Specific Gravity of some Liquefied Gases.** By ALBERT LADENBURG and C. KRÜGEL (*Ber.*, 1899, 32, 1415—1418).—Having been made acquainted with Dewar's researches on the subject (*Proc. Roy. Inst.*, 1896, 15, 138; compare *Proc.*, 1895, 11, 226), the authors have re-

determined the specific gravity of certain liquefied gases by weighing in the liquid a sinker, not of glass (compare this vol., ii, 208) but of silver (Dewar, *loc. cit.*); the results are now found to be more in harmony with his. Liquid oxygen has the density 1.134 (Dewar 1.1375); liquid ethylene, 0.6095; whilst a liquefied mixture of oxygen and nitrogen containing  $x$  per cent. of oxygen has the density  $d = 0.86 + 0.00289x$  (experimental numbers:  $d = 1.015, 1.068, 1.133$  when  $x = 53.6, 72.15, 94.4$  respectively).

By weighing sinkers of silver, ordinary glass, Jena glass and silver in succession in liquid air, and assuming the coefficient of expansion for silver given above, the mean coefficient of expansion between the ordinary temperature and that of liquid air (density 1.1215) boiling under atmospheric pressure was found to be 0.00003104 for ordinary glass, 0.00001822 for Jena glass.

C. F. B.

**New Apparatus for the Determination of Volume.** By CHARLES F. MCKENNA (*J. Amer. Chem. Soc.*, 1899, 21, 50—52).—An improved form of volumenometer of the Schumann or Candlot type. It consists of a flask of about 175 c.c. capacity with two vertical necks, one of which, having a diameter of about 5 mm., is graduated in tenths of a c.c., and closed at the top by a perforated stopper. The other tube, which is shorter, has a zero mark at about its middle point, on either side of which it is graduated for one or two c.c.; above the graduation, it expands to about 25 mm. diameter, and into it fits a perforated glass stopper, connected by means of a tube fitted with a stopcock with a rubber bulb. The mode of using is as follows. Liquid is introduced into the flask, the level in the shorter tube adjusted to zero by means of the rubber bulb, and the volume obtained by reading off the position of the liquid in the other limb. After removing the stopper from the shorter tube, the powdered solid is sifted in, the liquid adjusted to zero, and the volume again read off on the longer tube. The apparatus can be conveniently used with about 10 grams of material.

T. H. P.

**Composition of Mixed Vapours.** By HECTOR R. CARVETH (*J. Physical Chem.*, 1899, 3, 193—213).—In only a few exceptional cases does the vapour given off by a binary system possess the same composition as the liquid, and although of great importance in fractional distillation, the connection between the composition of the two phases has been little studied. A form of apparatus for the determination of the composition of the vapour is described, the principle of the method being that the condensed vapour is returned to a small receiver within the larger flask containing the solution whose boiling point is being taken, and in this receiver is made to boil. From this boiling point, the composition of the condensed vapour is determined by comparison with the boiling point curve of the two liquids. The cases examined were mixtures of (1) acetone and water, (2) benzene and carbon bisulphide, and the temperature | composition curves for liquid and vapour are given. The results obtained are verified by comparison with those derived from the direct analysis of the liquid volatilised between two temperatures sufficiently near to allow of a mean being taken. Brown's method of a constant temperature still-head

(Trans., 1881, **39**, 304) is inaccurate, as discrepancies are found in his results, the composition of the vapour being always displaced to the side of the more volatile compound. Purity of a compound is in general indicated by the identity of the boiling points of the liquid and condensed vapour. During the experiments, it was noticed that, in many cases where the composition of liquid and condensed vapour differ considerably, the Beckmann apparatus does not yield accurate results, differences of one degree being obtained by alteration of the rate of boiling.

L. M. J.

**Molecular Weights of Liquids. III.** By CLARENCE L. SPEYERS (*J. Amer. Chem. Soc.*, 1899, **21**, 282—287. Compare this vol., ii, 145).—From Leffeldt's vapour-pressure measurements (this vol., ii, 11), it is concluded that, in mixtures of benzene and toluene with carbon tetrachloride, both constituents have a normal molecular weight. When mixed with alcohol, however, both benzene and toluene are said to be highly polymerised, especially when the proportion of alcohol is small; the alcohol is regarded as highly polymerised in presence of a small proportion of toluene, but less so when the proportion is large; in benzene solution, the alcohol is regarded as being highly polymerised at all concentrations.

T. M. L.

**Continuous Change from Solid to Liquid.** By GEORGE A. HULETT (*Zeit. physikal. Chem.*, 1899, **28**, 629—672).—It having been suggested that crystalline-liquids are in a state approximating to the critical state (this vol., ii, 360), experiments were made to determine whether the heat of transition of the compounds becomes zero at higher pressures. The value of the heat of transition (that is, the change from crystalline-liquid to isotropic) is calculated from the lowering of the transition temperature by means of the expression  $L = 0.02n \cdot T^2/d$ , where  $d$  is the depression produced by  $n$  gram-molecules dissolved in 100 grams of the solvent, and  $T$  the absolute transition temperature. The temperatures were determined at pressures up to 300 atmospheres in the case of parazoxyanisole and parazoxyphenetole, and of solutions of thymol in these solvents. The latent heats of transition for parazoxyanisole thus found were  $L_0 = 4.33$  and  $L_{300} = 4.36$  cal.; and for parazoxyphenetole  $L_0 = 7.2$  and  $L_{300} = 6.6$  cal., so that the experimental pressures appear to be far removed from the critical pressure. The latent heat is also calculable from the volume change and the pressure coefficient of the temperature, but the values so calculated do not agree with the previous results, being far smaller. The cause of this difference is probably the solubility of the thymol in the crystalline-liquid, as not only the transition temperature, but also the melting point, is lowered by the addition of the thymol. The existence of a critical point for the solid crystalline-liquid was also investigated by the determination of the lowering of the melting point at various pressures, and application of the van't Hoff formula. The values so obtained were: parazoxyanisole,  $l_0 = 29$  cal.,  $l_{300} = 36.5$  cal.; parazoxyphenetole,  $l_0 = 14.7$ ,  $l_{300} = 22.3$  cal., so that the critical pressure appears to be a negative pressure of about 1000 atmospheres. For both compounds, the temperature range of the crystalline-liquid increases with



rise of pressure, so that a negative pressure is also indicated for the disappearance of this state. The pressure coefficients of the melting and transition points were also determined for pure cholesteryl benzoate, and from these, and the volume change, the heat of transition is calculated as 0.32 cal. The latent heat of fusion was also similarly determined for paratoluidine, benzene, and camphor, and in each case it was found to decrease with rise of pressure, the values obtained being: paratoluidine,  $l_0 = 39$ ,  $l_{300} = 37.1$ ; benzene,  $l_0 = 30.2$ ,  $l_{300} = 27.7$ ; camphor,  $l_0 = 9.4$ ,  $l_{300} = 8.0$  cal. From these, by subtraction of the external work, the internal heat of fusion is obtained, the difference being about 1 cal. in each case. The effect of pressure on the melting point was also investigated for many organic compounds, the temperature being found in all cases to be a linear function of the pressure, and the following values of the pressure coefficient in degrees per atmosphere were obtained: phenol, 0.0149; thymol, 0.0184; naphthalene, 0.0373; naphthylamine, 0.0200; benzophenone, 0.0289; stearic acid, 0.0258; crotonic acid, 0.0373; orthonitrophenol, 0.0240; phosphorus, 0.0290; menthol (m. p.  $36.5^\circ$ ), 0.0248; menthol (m. p.  $42.5^\circ$ ), 0.0245; monochloroacetic acid, 0.0147. The results for benzene, benzophenone, and phosphorus are shown to be in good accord with observations of Tammann, but the pressures were not carried sufficiently high to indicate curvature of the temperature | pressure curve.

L. M. J.

NOTE.—The results do not appear to agree with those of Damien (*Compt. rend.*, 1891, 112—785), who found in all cases a quadratic formula for the pressure effect. The difference is very marked for naphthylamine, for which Damien found a maximum melting point of  $50.5$  at 81 atmospheres, the value then decreasing to  $49.6$  at 173 atms., whereas the author obtains a steady rise from  $49^\circ$  to  $54.8^\circ$  at 300 atms., the value at 175 atms. being  $52.3$ .

L. M. J.

**Surface-tensions of Solutions of Alkali Chlorides.** By CHARLES E. LINEBARGER (*J. Amer. Chem. Soc.*, 1899, 21, 411—415).—The author has determined the relation between the surface-tensions and concentrations of solutions of lithium, sodium, and potassium chlorides. On constructing curves with surface-tensions as ordinates, and concentrations as abscissæ, it is seen that the curve for sodium chloride lies about midway between those for the potassium and lithium salts, the surface-tension being greater the smaller the molecular weight. If the concentrations be expressed in molecules per litre, the three curves become coincident. The surface-tension is not, as is generally supposed, a linear function of the concentration, as the curves show a slight convexity towards the axis of concentrations.

T. H. P.

**Ternary Mixtures.** By WILDER D. BANCROFT (*J. Physical Chem.*, 1899, 3, 217—231).—It has been shown by Taylor (*Abstr.*, 1897, i, 402), that in a ternary mixture of two non-miscible liquids with a third consolute liquid, the concentrations are connected by the relation  $(C_a A_a)^n = k C_b B_b$  where  $C_a$  and  $C_b$  are the concentrations of the consolute liquid, and  $A_a$  and  $B_b$  those of the other two liquids in

the two phases. Many cases of metallic ternary mixtures have been described by Wright (Abstr., 1891, 1158; 1893, ii, 15, 415, 522; 1894, ii, 419), and the author has examined the results in order to test their agreement with the above expression. The experimental errors were acknowledged by Wright to be great, but notwithstanding this, in some of the systems very fair constancy for  $k$  is obtained. In most cases, except where silver is the consolute metal, the distribution ratio is less than 2, and there appears to be no connection between the distribution ratio at great dilution and the reacting weights of the two metals. Thus in lead-zinc mixtures the ratio varies from 1.5 for tin as consolute to 39 for silver. The inexactitude of the experiments, however, makes further investigation desirable. L. M. J.

**Inversion of Sugar by Salts.** By LOUIS KAHLENBERG, D. J. DAVIS, and R. E. FOWLER (*J. Amer. Chem. Soc.*, 1899, 21, 1—23).—By determining the rate of inversion of sugar by the action of a number of colourless salts, firstly, from the polariscopic readings, and secondly, by calculating the number of molecules in the solution by means of the freezing point method, the authors show that the latter method gives reliable results. By this means, the rates of inversion have been measured for coloured salts with which accurate polariscopic determinations cannot be made. The results show that on arranging the metals according to the speed with which their analogous salts invert sugar solutions, the order is similar to that in the electrochemical series. To this general rule an exception is found in aluminium, the salts of which have relatively a very high velocity of hydrolysis; this may be due to the formation of a colloidal aluminium hydroxide, which would tend to aid the ionic dissociation of the salts and hence promote inversion of the sugar. Confirmation is given of Long's statement (Abstr., 1896, ii, 414, and 1897, ii, 547), to the effect that metallic chlorides invert sugar much more rapidly than the corresponding sulphates, owing to the ionising tendency of chlorine being greater than that of the  $\text{SO}_4$  complex. T. H. P.

**Nature of Valence.** By FRANCIS PRESTON VENABLE (*J. Amer. Chem. Soc.*, 1899, 21, 192—200 and 220—231).—The variation in the valency of an element is explained as due to the necessity for harmony between the motions of the combining atoms, which may be affected by temperature, light or electricity, or by the mutual influence of the atoms. T. M. L.

**The Boiling of Aqueous Colloidal Solutions.** By FRIEDRICH KRAFFT (*Ber.*, 1899, 32, 1584—1596).—The salts of the higher fatty acids behave as colloids in aqueous solution, but as crystalloids when dissolved in perfectly dry alcohol. In determining the boiling point of colloidal solutions, a difficulty occurs owing to the formation of bubbles, the tension of which materially increases the pressure on the boiling liquid; this can be largely overcome by using a deep layer of glass beads to break up the bubbles.

The addition of 7.88 grams of sodium palmitate to 30 grams of water raised the boiling point by only  $0.083^\circ$ , whilst if the molecule were dissociated in the ordinary way, a rise of more than ten times this

amount might be expected; a further addition of sodium chloride gave, however, a normal rise of temperature corresponding with  $M = 26.2$ , the value in pure water being 29.2. With sodium erucate there was a rise of  $0.017^\circ$  (partly due to 1 mm. increase of pressure) instead of  $0.200^\circ$ ; a further addition of sodium chloride gave a rise corresponding to  $M = 27$  instead of 29.2; in a second experiment, the rise of temperature was only  $0.001^\circ$  instead of  $0.295^\circ$ , and a subsequent addition of potassium bromide gave  $M = 68$  instead of 59.5. Sodium oleate caused no rise in temperature, although a rise of  $0.58^\circ$  should have occurred if the salt were dissociated in the ordinary way; subsequent addition of sodium chloride gave  $M = 30.8$  instead of 29.2. Potassium oleate gave a rise of  $0.005^\circ$  instead of  $0.328^\circ$ ; potassium erucate showed a fall of  $0.015^\circ$ , owing to a fall of 0.8 mm. pressure; potassium stearate gave a rise of  $0.015^\circ$  on adding 3.89 to 30 c.c. of water.

The values of  $M$ , when determined in anhydrous alcohol, were potassium formate, 87.60, theory 84.16; potassium acetate, 93.3, 94.9, 96.7, theory 98.18; sodium heptate, 180, theory 152.2; potassium heptate, 153.7, 156.5, 156.5, theory 168.3; sodium laurate, 237.2, theory 222.3; sodium myristate, 253, theory 250.3; sodium palmitate, 282.6, theory 278.4; sodium oleate, 301.3, theory 304.4. The presence of a small amount of water in the alcohol causes a very large increase in the values of  $M$ .  
T. M. L.

**Crystallisation of Colloidal Salt Solutions.** By FRIEDRICH KRAFFT (*Ber.*, 1899, 32, 1596—1608. Compare *Abstr.*, 1896, ii, 468).

—I. The temperature at which aqueous soap solutions gelatinise or deposit a solid soap is determined almost entirely by the melting point of the fatty acid contained in the soap. Thus dry sodium stearate melts at about  $260^\circ$ , but a 20 per cent. solution solidifies at  $69^\circ$ , a 15 per cent. solution at  $68^\circ$ , a 10 per cent. solution at  $68-67^\circ$ , and a 1 per cent. solution at  $60^\circ$ , the melting point of stearic acid being  $69.4^\circ$ . Dry sodium palmitate melts at  $270^\circ$ , but a 20 per cent. solution solidifies at  $62-61.8^\circ$ , and a 1 per cent. solution at  $45^\circ$ , the melting point of palmitic acid being  $62^\circ$ . Dry sodium myristate melts at  $250^\circ$ , but a 20 per cent. solution solidifies at  $53-52^\circ$ , and a 1 per cent. solution at  $31.5^\circ$ , the melting point of myristic acid being  $53.8^\circ$ . Dry sodium laurate melts at  $255-260^\circ$ , but a 25 per cent. solution solidifies at  $45-42^\circ$ , a 20 per cent. solution at about  $36^\circ$ , and a 1 per cent. solution at about  $11^\circ$ , the melting point of lauric acid being  $43.6^\circ$ . The agreement between the melting point of the fatty acid and the temperature at which the sodium salt solidifies from the solution is most marked among the highest homologues, and it is here also that the concentration has least influence on the temperature of solidification.

Similar results are found in the unsaturated series. Dry sodium oleate melts at  $232-235^\circ$ , but a 25 per cent. solution solidifies at  $13-6^\circ$ , the melting point of oleic acid being  $14^\circ$ . Dry sodium elaidate melts at  $225-227^\circ$ , but a 20 per cent. solution solidifies at  $45.5-44.8^\circ$ , the melting point of elaidic acid being  $45^\circ$ . Dry sodium erucate melts at  $230-235^\circ$ , but a 20 per cent. solution solidifies at  $35-34^\circ$ , and a 1 per cent. solution at  $27^\circ$ , the melting point of erucic acid being  $34^\circ$ .

Dry sodium brassidate melts at  $245-248^{\circ}$ , but a 20 per cent. solution solidifies at  $56^{\circ}$ , the melting point of brassidic acid being  $60^{\circ}$ .

In explanation of these observations, it is suggested that when it is dissolved in water, the soap is completely hydrolysed into caustic soda and a fatty acid. The fatty acid is not soluble by itself, but is held in solution by the caustic soda, and the molecules of the fatty acid and base are regarded as grouped into large molecular complexes, giving rise to *colloidal* solutions, as has been shown in the preceding abstract. These colloidal solutions can only exist above the melting point of the fatty acid, but in the lower homologues the melting point is lowered by partial miscibility with water and the soap solution solidifies at a lower temperature, especially when dilute. Crystallisation occurs least readily when the alkali of the soap has a great affinity for water. Thus potassium soaps remain gelatinous at a much lower temperature than sodium soaps; on the other hand, lithium soaps are almost insoluble owing to the feeble affinity of the base for water.

An attempt is made to extend these observations to the hydrochlorides of feeble bases. It is shown that hexadecylamine hydrochloride, which decomposes at  $150^{\circ}$  when dry, crystallises from a 20 per cent. aqueous solution at  $45-42^{\circ}$ , the free base melting at  $46^{\circ}$ . A number of other cases are given, but there does not appear to be any marked relationship between the melting point of the base and the temperature at which the salt solutions crystallise, the discrepancy being perhaps due to the solubility of the amine.

II. 'The crystallisation of salts results from a disturbance of the system present in the solution; the effects of this disturbance are less marked the lower the temperature at which the crystallisation takes place.' Colloidal solutions deposit globular aggregates, and the author has therefore assumed (*loc. cit.*) that such solutions have a concentric configuration or form of motion. It is now shown that certain crystalloids can be made to separate in globular forms by careful over-cooling, and it is therefore assumed that these solutions also possess a concentric structure.

T. M. L.

**Colloidal Salts as Membrane-formers in Dyeing.** By FRIEDRICH KRAFFT (*Ber.*, 1899, 32, 1608—1622).—"Dyeing in the great majority of cases consists in the separation of colloidal salts on or in the fibre." Colours of low molecular weight and small dyeing power are also devoid of colloidal properties, and are converted into true dyes by means of a colloidal mordant, tannin, or an insoluble soap for basic colours, and a metallic hydroxide for acid colours. On the other hand, the azo-dyes of high molecular weight, which dye cotton without a mordant, are sparingly soluble colloids which either separate directly on the fibre or are 'salted out' into it.

Rosaniline hydrochloride, methyl-violet, and methylene-blue have a normal molecular weight in dry alcohol according to the boiling point method, but give values about twice as great in aqueous solution, thus giving an indication of feeble colloidal properties. Thus, rosaniline hydrochloride ( $M=337$ ) gave 330.5, 325, and 343.6 in alcohol, but 520.6, 589.9, and 617.0 in water; methyl-violet (407.9) gave 403.5, 403.5, and 421.1 in alcohol, but 804.5, 838.7, and 870.4 in

water; methylene-blue (319·8) gave 321·4 and 342·7 in alcohol, but 442 in aqueous alcohol, and 321·2, 492·4, and 530·5 in water.

The colloidal nature of tannin is shown by the freezing point of its aqueous solution, which gave  $M=1587$  and 1626, calculated value = 322; a diffusion experiment showed a similar result. The metallic hydroxides used as mordants are true colloids, as was shown by Graham, (*Annalen*, 1862, 121, 1). A colloidal solution containing 3·38 per cent. of ferric hydroxide and 0·098 per cent. ferric chloride was found to freeze within  $0\cdot001^{\circ}$  per cent. of the freezing point of pure water; on cooling to  $-16^{\circ}$ , the hydroxide separated in thin, glistening, dark red-brown flakes. A colloidal solution containing 0·5 per cent. of aluminium hydroxide had exactly the freezing point of pure water; on cooling to  $-16^{\circ}$ , the hydroxide separated in very lustrous, transparent films. The insoluble soaps of iron, chromium, aluminium, tin, and antimony are also regarded as colloids, since they are precipitated in "globomorphous" form. It is shown that methylamine palmitate acts like the alkali soaps and gives colloidal solutions; the palmitates, &c., of basic dyes are therefore regarded as insoluble soaps, and colloidal in nature. In support of this, it is shown that rosaniline caproate at first lowers the boiling point of water to a small extent, owing to the volatility of the caproic acid, but on adding a further quantity, a very slight rise is observed, corresponding with a molecular weight of at least 600. The colloidal nature of the tannates of rosaniline, methylene-blue, chrysoidine, auramine, and a number of other mordanted dyes is assumed from the "globomorphous" form in which they are precipitated.

It is further shown that benzopurpurin which dyes cotton directly, gives a value  $M=3000$ , the calculated value being 724. On the other hand, "diamine pure blue" gives only  $M=343$ , instead of 993. The colloidal nature of these dyes is, however, shown by the fact that whilst rosaniline hydrochloride, methyl-violet, and methylene-blue diffuse through parchment, benzopurpurin, benzazurin, and azo-blue are retained.

T. M. L.

**Angles of Contact between the Crystal Faces of Alum and its Saturated Solutions.** By A. ROTA (*Real. Accad. dei Linc.*, 1898, 7, 125—129).—In order to find a connection between the physical properties of a salt solution and the habit of the crystals separating from that solution, the author has determined the angle of contact between octahedral and cubic alum crystals and their saturated solutions. On allowing the solvent to evaporate from a solution of pure alum in distilled water, octahedral crystals are deposited; and by heating powdered alunite at  $300-400^{\circ}$ , and extracting with water the reddish substance thus produced, a solution is obtained which on purification yields cubic alum crystals. When the small crystals obtained by the spontaneous evaporation of the solutions were suspended in their respective mother liquors and allowed to grow, uneven faces giving irregular reflections were the result; so that before using the crystals, the faces were carefully polished, care being taken to keep the polished faces parallel to the original face. The method of measurement employed was that devised by Quincke, in which a drop of the liquid is placed on a plane surface of the solid and the angle between the light-ray reflected from the last element of the

liquid and that from the surface of the solid is read off on a goniometer. The angles of contact between an octahedral face and the octahedral and cubic solutions respectively were found to have the mean values  $10^{\circ} 16'$  and  $15^{\circ} 13'$ , and the values for a cubic face and the cubic and octahedral solutions respectively,  $10^{\circ} 22'$  and  $15^{\circ} 36'$ . From this, it is concluded that from any solution that form crystallises whose faces present the least angle of contact with the solution. T. H. P.

#### Vacuum Regulator for Distillations Under Reduced Pressure.

By VICTOR AUGER (*Bull. Soc. Chim.*, 1898, 19, [iii], 731—733).—This apparatus consists of a reservoir separated into two parts by a horizontal indiarubber membrane, each enclosure being separately connected with the vacuum pump. The lower enclosure is connected with the distillation apparatus and contains the manometer; it is also fitted with an automatic arrangement for introducing variable quantities of air into the apparatus. This consists of a hollow nickel tube open at both ends, which is inserted horizontally into the reservoir by means of a flexible rubber stopper. The end of the tube within the apparatus is flattened out into a disc which is placed immediately below the indiarubber membrane; the outer end is bent downwards at right angles, and is pressed against an indiarubber pad by means of a counterpoise. At the commencement of the operation, the pressure in both compartments of the reservoir is diminished to the required extent, and the upper enclosure is then cut off from the pump, and as the pressure in the lower compartment continues to fall the membrane becomes convex on its lower side and presses down the disc of the hollow nickel tube. The outer end of this tube is consequently lifted off its indiarubber pad, and a certain quantity of air rushes into the lower receptacle, the pressures on each side of the diaphragm are equalised, and the membrane and nickel lever resume their original positions. This automatic introduction of air is repeated whenever the pressure in the lower receptacle falls below that in the upper; the apparatus maintains a constant pressure as long as the volume of gas removed by the pump exceeds that generated in the distillation. G. T. M.

**Modifications of the Geissler Pump.** By GIOVANNI GUGLIELMO (*Real. Accad. dei Linc.*, 1898, 7, 240—249).—The author describes further improvements in the modified form of Geissler's pump already devised by him (*Abstr.*, 1891, 524). The long, straight tube of the Geissler pump is replaced by a flexible rubber tube, the height of the instrument thus being diminished. To economise mercury and facilitate the manufacture of the pump, the bulbs are made of small capacity. The pressure of the rarefied air is measured by determining the pressure necessary to compress all the air in the receiver into the small capillary boring of the stopcock, the relation between the two pressures being previously found. T. H. P.