

General and Physical Chemistry.

Refractive Indices of Crystallised Alums. By C. SORET (*Compt. rend.*, **99**, 867—869).—By means of the instrument previously described (*Compt. rend.*, **95**), the author has determined the refractive indices of many alums for the lines *a*, B, C, D, E, *b*, F, G, of the solar spectrum. He has also determined the specific gravities of the alums by means of the hydrostatic balance. In the following table, only the refractive indices for D and the specific gravities are given :—

	n_D .	Sp. gr.
Ammonium aluminium alum	1·45939	1·631
Sodium " "	1·43884	1·667
Methylamine " "	1·45410	1·568
Potassium " "	1·45645	1·735
Rubidium " "	1·45660	1·852
Cæsium " "	1·45856	1·911
Thallium " "	1·49748	2·257
Ammonium indium " "	1·46636	2·011
" gallium " "	1·46552	1·745
Potassium " "	1·46499	—
Ammonium chromium " "	1·48418	1·719
Potassium " "	1·48137	1·817
Rubidium " "	1·48151	1·946
Thallium " "	1·52280	2·236
Ammonium iron " "	1·48482	1·713
Potassium " "	1·48169	1·806
Rubidium " "	1·48234	1·916
Cæsium " "	1·48378	2·061
Thallium " "	1·52365	2·385

The molecular volume is not constant for the different terms of the same series, but it seems to vary in a definite manner for the corresponding terms of the aluminium, chromium, and iron series.

In passing from one alum to another, the variation in the refractive index is sensibly the same in the three series, thus following a law which has been observed in other series of compounds. It is worthy of note, however, that the refractive index of sodium alum is much less than that of potassium alum, whilst in the case of the chlorides the sodium salt is intermediate between the potassium and ammonium compounds.

The author's value for the refractive index of thallium alum is much higher than that obtained by Fock.

Methylamine alum is intermediate between the sodium and potassium compounds, and it would seem as if, in the aluminium series, the refractive index varied continuously with the molecular weight of the alkaline radicle.

C. H. B.

Inversion of the Electromotive Force of a Copper Iron Junction at a High Temperature. By F. F. LE ROUX (*Compt. rend.*, **99**, 842—844).—A bar of iron was bent in the form of a horse-shoe, and attached at each end to a copper bar. This couple was placed in a furnace and heated nearly to the melting point of copper, a current of about 350 ampères being passed through the couple. Any change in the temperature of the junction was detected by observing a change in the relative luminosity of the junction, the results of ocular observation being confirmed by the action of the radiation on a gelatino-bromide plate.

It was found that at about 1000° a current passing from the copper to the iron raises the temperature of the junction, whilst at the ordinary temperature a current in the same direction cools the junction.

C. H. B.

Electrolysis of Silver Fluoride, Chlorate, and Perchlorate. By G. GORE (*Chem. News*, **50**, 150).—A moderately strong solution of silver fluoride acidified with hydrochloric acid is a very good conductor of electricity, and is very readily decomposed by means of silver electrodes and a current from a cell containing zinc and platinum in dilute sulphuric acid. Crystals of silver are rapidly deposited at the cathode, whilst the anode soon becomes rough, grey in colour, and very friable. In special experiments, no evidence could be obtained to show that this loss of cohesion was due to the diffusion of liberated fluorine through the silver.

When a solution of silver chlorate is electrolysed by sheet silver electrodes and a current from two Smee's cells charged with very dilute sulphuric acid (1 vol. of acid to 50 of water), conduction is good, and silver is freely deposited only at first; the deposit being loose, and not very white. The anode also is soon coated with a black film, presumably silver peroxide, which seems to stop the current; it is permanently blackened, although but slowly corroded. With one Smee's cell, the deposit is formed slowly, and is more coherent. This solution requires a feeble current, a large cathode, and a much larger anode.

When silver perchlorate is similarly electrolysed, conduction is very good, and loose, bulky, silky crystals of silver are soon deposited at the cathode, whilst the anode quickly becomes black, the current at the same time becoming much diminished. With one cell and a more dilute solution, conduction is free, the deposit is smaller, and the anode becomes less dark. A silver wire anode soon becomes corroded and loosely coated with a black substance; this falls off and is ultimately replaced by a thick green coating; no gas is evolved. The solution requires a large cathode and a rather small anode.

D. A. L.

Electro-deposition of Carbon and Silicon. By G. GORE (*Chem. News*, **50**, 113—114).—Carbon, silicon, and boron have each been deposited during the electrolysis of certain fused mixtures.

Carbon is deposited when a current from 10 Smee's elements is passed through a fused mixture of 200 grains of sodium hydroxide, 170 grains precipitated silica, and 610 grains of mixed anhydrous sodium and potassium carbonates, the anode being sheet platinum,

the cathode a wire of the same metal; the deposition of carbon is, however, probably due to a secondary reaction of this character: silicon is first deposited and this reacts with the alkaline carbonates, and causes the separation of carbon. The same phenomenon occurs when a mixture of 475.2 grains of 97.1 per cent. sodium carbonate and 217.4 grains sodium borofluoride is similarly treated, and apparently also in the electrolysis of aqueous or alcoholic oxalic acid. The deposited carbon is not crystalline.

Carbon is not deposited either during the electrolysis of sodium and potassium carbonates, using eight Smee's cells and platinum electrodes at a red heat, or when boric acid is included in the mixture, or by the electrolysis of any of the following: potassium cyanide, oxalic acid in solution in hydrochloric or nitric acid, sodium formate or formic acid, carbonic oxide and anhydride, pyrogallol, liquid hydrocyanic acid saturated with carbonic oxide, fuming sulphuric or syrupy phosphoric acids saturated with dry carbonic anhydride; or from dilute sulphuric acid over which coal-gas was passing during the 14 days the electrolysis was continued. Carbon tetrachloride does not yield carbon under the influence of an electric current. These experiments were conducted under different conditions as to strength of current, length of time, temperature, and composition of electrodes.

Silicon is deposited when a fused mixture of 300 grains of 97.1 per cent. potassium carbonate and 442 grains of potassium silicofluoride is electrolysed, as described above in the carbon-deposition experiments.

D. A. L.

Relation between the Ordinary Thermometer and the Weight Thermometer. By E. BARBIER (*Compt. rend.*, 99, 752—753).—A demonstration of the theorem that if the ordinary thermometer and the weight thermometer agree at the two fixed points, they agree at all temperatures.

C. H. B.

Attraction of Homogeneous Molecules. By C. SCHALL (*Ber.*, 17, 2555—2577).—In order to interpret experiments on the relation between the rates of evaporation of liquids and their molecular weights and heats of expansion, the author has more particularly studied the phenomena of cohesion and adhesion of liquids, a subject of interest to the chemist as dealing with the attraction of homogeneous and heterogeneous molecules. The method of investigation was based on that of the so-called adhesion plates, which consists, in outline, in suspending a plate of glass from one pan of a balance, and counterpoising it; the plate being adjusted to a level, a dish containing the liquid to be examined is placed under it, and then raised until the surfaces of the liquid and glass are in contact. To the opposite pan of the balance, weights are added until the glass is severed from the liquid; this excess of weight is then noted. The apparatus used, together with devices for levelling the plate and for the complete severance of the liquid and glass, are described in detail in the paper. As the attractive force between two contingent molecules within a liquid is proportional to their mass and inversely proportional to the square of the distance between them, and as increase of distance is correlative with decrease of specific gravity and also with that of cohesion,

it follows that a decrease of the latter caused by warming the liquid is proportional to the square of the former. But the superficial expansion, which is equal to the $\frac{2}{3}$ power of the cubical, is inversely proportional to the specific gravity. As the superficial expansion increases, the number as also the mass of molecules under the plate and their correlative cohesion diminishes, and therefore the latter diminishes in direct proportion to the $\frac{2}{3}$ power of the specific gravity. Hence if s and s_1 be the specific gravities for any two degrees of temperature, G and G' the excess of weight necessary for the disruption of the plate, then

$$G = G' \left(\frac{s}{s_1} \right)^2 \left(\frac{s}{s_1} \right)^{\frac{2}{3}}.$$

Experimental results are tabulated which demonstrate the validity of the formula, and of the law deduced therefrom, that the force by which homogeneous molecules are attracted varies in direct proportion to the square of the specific gravity, and also to the mass of the molecules. From the experimental results can be deduced the diminution of cohesion for each degree of temperature, and thus the critical point at which the cohesion is *nil*.

But the results obtained with some of the liquids examined, especially water, benzene, and its derivatives, are not in strict accordance with the law enunciated above, so that it would appear that the force of cohesion is dependent to some extent on the chemical constitution of the liquid. In the case of two liquids, it is further demonstrated that the relation between the respective cohesions and also their specific gravities at boiling points within restricted limits of pressure are approximately identical.

These experiments are also of importance in regard to the phenomenon of capillary attraction, a force which depends on the difference between the force of cohesion of the molecules of the liquid with one another, and of adhesion to the molecules of the glass. If the force of attraction as represented by the capillary height = h , that of the adhesion of the liquid to the glass = a , and of the cohesion of the liquid = c , then—

$$h = a - c.$$

The form of the meniscus is concave if $a > c$, but convex if $a < c$. But from the above formula, $\frac{a}{a'} = \left(\frac{s}{s'} \right)^2 \left(\frac{s}{s'} \right)^{\frac{2}{3}}$, then if the capillary heights are h and h' at two different temperatures, then $h = a - c$, and $h' = a' - c'$, it follows that $h' = \frac{a-c}{\left(\frac{s}{s'} \right)^2 \left(\frac{s}{s'} \right)^{\frac{2}{3}}}$, or $h' = \frac{h}{\left(\frac{s}{s'} \right)^2 \left(\frac{s}{s'} \right)^{\frac{2}{3}}}$.

Experimental results are also adduced in support of these formulæ, although water and liquid sulphur offer instances of marked exception; it is thus probable that the molecular constitution of these liquids is the cause of the discrepancy.

V. H. V.

Relation between Molecular Weight and Velocity of Evaporation of Liquids. By C. SCHALL (*Ber.*, 17, 2199—2212).—This

paper contains a description of the apparatus and method of working employed by the author in his experiments with benzene, carbon bisulphide, and water (Abstr., 1884, 551).

Experiments with substances of nearly coincident molecular weight and boiling point:—

	Calculated.	Found.
{ Phenol	$m = 94$	95·57, 95·11, 95·11
{ Aniline	$m = 93$	91·48, 91·91, 91·91
{ Toluene	$m = 92$	93·85
{ Valeraldehyde	$m = 86$	84·3
{ Monochlorobenzene	$m = 112·5$	108·2
{ Acetic anhydride	$m = 102$	106
{ Benzoic chloride	$m = 140·5$	144·3, 144·5
{ Ethyl benzoate	$m = 150$	145·7, 145·2

Experiments with substances of nearly equal molecular weights, but of different boiling points:—

	Calculated.	Found.
{ Ethyl acetate	$m = 88$	86·32, 87·76
{ Amyl alcohol(fermentation)	$m = 88$	89·71, 87·76
{ Benzaldehyde	$m = 106$	104·7, 110
{ Acetic anhydride	$m = 102$	103·3, 98·27

Experiments with substances of unequal molecular weights, but of nearly coincident boiling points:—

	Calculated.	Found.
{ Acetic chloride	$m = 78·5$	78·06
{ Acetone	$m = 58$	58·33
{ Alcohol	$m = 46$	41·2, 41·2
{ Benzene	$m = 78$	87·12, 87·12
{ Toluene	$m = 92$	94·28
{ Phosphorus oxychloride ..	$m = 153·5$	149·8

Substances with different boiling points and different molecular weights:—

	Calculated.	Found.
{ Benzene	$m = 78$	75·5, 75·5
{ Toluene	$m = 92$	95·04, 95·04
{ Methyl alcohol	$m = 32$	30·66
{ Propyl alcohol	$m = 60$	62·63
{ Ethyl alcohol	$m = 46$	45·48
{ Isobutyl alcohol	$m = 74$	74·84
{ Isobutyl alcohol	$m = 74$	65·65
{ Amyl alcohol(fermentation) ..	$m = 88$	99·19

Recent determinations of heats of vaporisation show that these are proportional to the time of vaporisation. In the following table, t is the boiling point at which the heat of vaporisation L was determined, DL the product of the latter multiplied by the theoretical density, m the calculated, and m' the found molecular weight:—

	<i>t.</i>	L.	DL.	<i>m.</i>	<i>m'.</i>
Water.....	100°	532·0 cal.	331·7	—	—
Wood spirit.....	66·5°	261·7 „	290·1	32	36·6
Ethyl alcohol.....	7·8	206·4 „	328·8	46	46·4
Amyl alcohol.....	131	120·0 „	368·7	88	89·0
Ethyl acetate.....	74	105·0 „	320·0	88	91·2
Methyl butyrate....	93	86·0 „	303·8	102	111·2
Oil of lemon.....	165	69·5 „	327·4	136	138·3
Oil of turpentine...	156	68·5 „	322·7	136	139·8
Butyric acid.....	164	114·0 „	347·5	88	84·0
Ethyl valerate.....	113·5	68·4 „	308·0	130	140·0

The author has further compared the velocity of evaporation of acetic acid with that of toluene, amyl alcohol, and isobutyl alcohol, and the results obtained show that the molecular weight of acetic acid at its boiling point is 89·8. This may also be calculated from Favre and Silbermann's determinations of its heat of vaporisation, and likewise for formic acid, the molecular weight 69.

A. K. M.

On Crystallisation. Observations and Conclusions. By G. BRÜGELMANN (*Ber.*, 17, 2359—2372).

Stability of Compounds. By W. ALEXÉEFF (*Jour. Russ. Chem. Soc.*, 16, 641—642).—The author communicates his researches as to the conditions determining the stability of a compound in the presence of an excess of one or the other of its constituents. The results agree with what he found with regard to the stability of hydrates of alcohols in their aqueous and alcoholic solutions. The difference in the stability of hydrates determines the difference of the vapour-tensions, at one and the same temperature, for two solutions, which are formed by water, and a liquid capable of yielding a hydrate. Moreover, in an aqueous solution, this tension is always smaller when the formula of the hydrate is $A + nH_2O$, n being generally greater than unity. With solutions formed by water and ether, a difference in temperature of 8° corresponds with equal tensions. B. B.

Phenomena of Condensation. By D. MENDELÉEFF (*Jour. Russ. Chem. Soc.*, 16, 643—644).—The author remarks that the phenomena of condensation, as shown in the case of the formation of solutions or on diluting some liquids, is analogous to what takes place when spherical bodies of different diameters, such as samples of different seeds (pease and millet), are mixed together. When spherical bodies are mixed, as may be shown by experiment or by geometrical analysis, the weight of a measure containing a large number of such small spheres of both kinds is greater than the mean calculated from the weight of both kinds taken alone. In the same manner, the sp. gr. of a solution is greater than it should be, when calculated from the sp. gr. and the quantity of the constituent liquids. The analogy in the change of volumes which takes place in both the above cases shows that when a

small bulk of light spheres of small diameter is added to heavier spheres of large diameter, the sp. gr. of a cubic measure of the last may become greater, exactly as the first addition of water to normal sulphuric acid raises its sp. gr. The above geometric question is, unfortunately, up to the present inaccessible for full geometric analysis, and the experimental investigation is rendered very difficult by the impossibility of obtaining the necessary balls of regular size and equal diameters.

Experiments with mixtures of millet and gunpowder, however, have convinced the author that the above phenomenon exists, but it is only a statical representation of a dynamical phenomenon which takes place in the case of dissolution as a simple act of chemical association of heterogeneous particles.

B. B.

Connection between Pseudo-solution and True Solution.

By W. W. J. NICOL (*Chem. News*, 50, 124).—Arguing from the molecular theory of solution, according to which the dissolution of a salt in water is the result of the attraction of the water molecules for a single salt molecule exceeding that of the attraction of the salt molecules for one another, the author demonstrates that the difference between pseudo-solution and true solution lies only in the degree of subdivision of the solid. For by this theory dissolution depends greatly upon cohesion, and where cohesion is small dissolution is easy, and *vice versa*; taking barium sulphate as an example, the cohesion is great, the solubility almost *nil*; if, however, the cohesion is diminished by any means, then the finely-divided salt will remain suspended in water for a long time, that is, in a state of pseudo-solution, which shows that the water molecules alone were not able to overcome the cohesion, but this being to a certain extent overcome, *pseudo-solution* is the result. Supposing now the insoluble salt could be resolved into its molecules, that is, further subdivided, then it is easy to conceive that it would be possible to dissolve it to a great extent in water, and produce a *true solution*, from which the solid would separate but slowly, owing to the solid molecules seldom coming in contact in sufficient numbers for their mutual attraction to overcome that of the water for them. As examples of such cases, the author refers to the fact that many almost insoluble compounds are precipitated with extreme slowness from cold dilute solutions.

D. A. L.

Rise of Solutions in Capillary Tubes.

By M. GOLDSTEIN and A. DAMSKI (*Jour. Russ. Chem. Soc.*, 16, 642—643).—According to Valson, the rise of a large number of solutions of salts in capillary tubes is inversely proportional to their specific gravities. This erroneous conclusion is explained by the fact that Valson worked with solutions showing no great differences in sp. gr. and, therefore, in the rise. Very different results are obtained on using solutions of great concentration (2 or 3 gram-mols. of salt to 1 litre of water) and narrower tubes; here the specific gravities and rise in the tubes differ conspicuously from those of pure water, and the regularity, shown by Valson, does not exist, *e.g.* :—

	Height of rise. <i>h.</i>	Sp. gr. <i>d.</i>	<i>h.d.</i>
Pure water	118·2	1·000	118·2
KCl $\frac{1}{4}$ mol. wt. to 1 litre	117·4	1·009	118·4
” $\frac{1}{3}$ ” ” ..	117·3	1·016	119·1
” $\frac{1}{2}$ ” ” ..	116·4	1·025	119·3
” 1 ” ” ..	115·3	1·048	120·8
” 2 ” ” .	114·1	1·100	125·5
” 3 ” ” ..	112·4	1·155	129·8

The value *h.d* equals that for water only for very dilute solutions.

The determinations of the above values for potassium chloride, bromide, and iodide have shown that the rise of solutions of potassium bromide of different degrees of concentration is the mean of the rise of corresponding solutions of potassium iodide and chloride, the molecular weight of KBr being the mean between those of KCl and KI:—

Solutions.	KCl. <i>a.</i>	Height of rise.		KBr.	
		KI. <i>b.</i>	calc. from		found <i>c.</i>
			$\frac{a+b}{2} = c.$		
$\frac{1}{4}$ mol. in 1 litre..	117·4	—	—	115·9	
$\frac{1}{3}$ ” ..	117·3	114·5	115·5	115·2	
$\frac{1}{2}$ ” ..	116·4	113·0	114·7	114·6	
1 ” ..	115·3	108·5	111·9	111·3	
2 ” ..	114·1	100·2	107·1	107·1	
3 ” ..	112·4	93·5	102·9	102·8	

B. B.

Capillary Phenomena in Relation to Constitution and Molecular Weight. By J. TRAUBE (*Ber.*, 17, 2294—2316).—All the experiments described in this paper were made with *aqueous* solutions of organic substances: the advantages of the use of such solutions over organic liquid compounds, being the much greater height at which the former stand in capillary tubes, and the much greater differences in capillary height shown in the case of closely related substances. Voluminous tables are given, at once showing the difference in capillary height caused by difference in the concentration of solutions of the same substance, and comparing the capillary heights of unlike substances in solutions of the same degree of concentration. The following are amongst the more important conclusions drawn from these experiments:—1. The capillary height of the solution of an organic body decreases with increasing concentration. Equal differences of height are not, however, caused by equal increments of concentration, the rate of difference first attaining a maximum, and then diminishing. 2. In a homologous series, the capillary height diminishes with increasing molecular weight. The difference reaches its maximum sooner in more concentrated than in more dilute solutions. 3. Isomeric substances, although of related constitutions, have not necessarily equal capillary heights. With regard to the capillary relations of different organic series, the author gives

the following as the result of his observations:—An increase in capillary height is observed in passing, 1, from the fatty alcohols to the corresponding aldehydes or acids; 2, from the fatty acids to the hydroxy-acids; 3, from the monohydric to the di- and tri-hydric alcohols; 4, from the normal and iso-alcohols to the tertiary alcohols; 5, from the ethereal salts of formic acid to isomeric ethereal salts of the higher fatty acids; 6, from compounds of the propyl series to those of the allyl series. Probably an increase in capillary height also occurs in passing from aldehydes to isomeric ketones, and from fatty acids to their monosubstituted halogen-derivatives, although on further substitution a decrease occurs; further observations are required on these two points. Aldehydes show a lower capillary height than the corresponding fatty acids in concentrated solutions, but in dilute solutions the reverse is observed. Normal alcohols show a lower capillary height than iso-alcohols in concentrated solutions.

A. J. G.

Mutual Relations of the Physical Properties of the Elements. By H. FRITZ (*Ber.*, 17, 2160—2165).—This paper contains a table of most of the heavy metals, with their melting points, specific gravities, atomic weights, and specific heats; from these, it may be shown by calculation that the product of the atomic heat by the relative heat is equal to the cube root of the product of the melting point multiplied by the specific heat, $As \cdot Ds = \sqrt[3]{ts}$; A being the atomic weight, s the specific heat, D the sp. gr., and t the melting point. The elements are arranged in groups in which different values are substituted for t . In the case of lithium, sodium, and potassium, the value $\frac{t + 50}{2.50}$ is substituted for t ; in the case of magnesium and

aluminium the value $\frac{t + 50}{7.4}$, and in that of strontium and barium $\frac{t + 50}{30}$.

If the metals be arranged I, according to the amount of heat liberated by their union with oxygen and chlorine, and II, according to their conductivity for heat, the one series will be found to be the reverse of the other.

A. K. M.

A General Statement of the Laws of Chemical Equilibrium.

By H. LE CHATELIER (*Compt. rend.*, 99, 786—789).—The author extends and modifies Van t'Hoff's general statement of the chemical equilibrium of a system by including in it the "condensation" of the system, that is, pressure, concentration, number of molecules in unit volume, &c., and by giving it a form similar to that of the laws relating to changes of equilibrium which effect mechanical work. Reversible chemical changes are thus brought into the class of reciprocal phenomena.

When a system in stable chemical equilibrium is acted on by an external cause which tends to alter the temperature or condensation either of the whole system or of some of its parts, the system can only

undergo such internal modifications as would, if they had taken place spontaneously, have produced a change of temperature or condensation of the contrary sign to that resulting from the action of the external cause.

These modifications are generally progressive and incomplete. They are, however, sudden and complete if they can take place without changing the individual condensation of the different homogeneous parts of the system, whilst at the same time they alter the condensation of the system as a whole.

They are *nil* when their occurrence cannot produce changes analogous to those due to the external cause.

Although modifications may be possible, they do not necessarily take place. In cases where no change occurs and the system remains unaltered, the original stable equilibrium becomes unstable, and the system can then only undergo such modifications as tend to bring it back to stable equilibrium. Many well-known reactions, including the phenomena of fusion, evaporation, solution, &c., are cited as examples.

C. H. B.
