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PROGRESS OF CHEMISTRY.

GENERAL AND PHYSICAL CHEMISTRY.

Specific Heats.

The molecular heat of hydrogen from 0—2600° abs. has been calculated¹ on the basis of Bohr's model of the hydrogen molecule and the assumption that the rotational energy corresponds with *three* degrees of freedom. The molecular energy of gases has been discussed² from the point of view of dynamical theory. The increase of specific heat on rise of temperature is assumed to be due to vibrations between the atoms, to which the principle of equipartition does not apply. Equipartition of energy is assumed between each degree of freedom of translation and each effective degree of freedom of rotation. The abnormal behaviour of hydrogen at low temperatures³ is supposed to be due to a change of molecular structure which deprives the molecule of its two degrees of freedom of rotation. In tri- and poly-atomic gases there is generally a considerable amount of energy of vibration. The conclusion is drawn that the quantum theory is unnecessary, but that the observed facts are not in conflict with it.

The specific heat of nitrogen at 92° abs., corrected for deviations from the gas laws, is almost exactly the equipartition value.⁴ The value of dC_p/dp is 0.300 cal./atm.

The velocity of sound in a dissociating gas, such as $N_2O_4 \rightleftharpoons 2NO_2$, has been calculated.⁵ It depends on the reaction velocity coefficients, and the latter may be determined in this way.

The internal energy of solids from the point of view of atomic

¹ F. H. MacDougall, *J. Amer. Chem. Soc.*, 1921, **43**, 23; *A.*, ii, 238.

² (Sir) J. A. Ewing, *Proc. Roy. Soc. Edin.*, 1920, **40**, 102; *A.*, ii, 299.

³ Eucken, *A.*, 1912, ii, 232.

⁴ R. Bartels and A. Eucken, *Z. physikal. Chem.*, 1921, **98**, 70.

⁵ A. Einstein, *Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1920, 380; compare F. Keutel, *Diss.*, Berlin, 1911.

structure has been considered.⁶ Further measurements of specific heats at low temperatures have been determined with a modified form of Nernst and Schweser's apparatus.⁷ The results are in most cases in good agreement with Debye's formula.⁸ The velocity of sound in air, nitrogen, carbon dioxide, methane, and ethane, at temperatures up to 1000° has been determined by a direct method.⁹ The true molecular heats at constant volume are calculated: air $4.8 + 0.0004T$; nitrogen $4.775 + 0.00042T$; carbon dioxide $6.30 + 0.00205T + 0.0000007T^2$; methane $6.66 + 0.019t$; ethane $9.04 + 0.0183t$.

The difference of the molecular heats of a gas has been calculated by three new equations: ¹⁰ $C_p - C_v = 0.000087/d_c v_c = 0.0935L/T' = 0.0935p_c/T_c d_c$. The symbols denote: critical density d_c , critical volume v_c , critical temperature T_c , boiling point T' , latent heat L , and the third equation is derived from the relation $L = p_c T' / T_c d_c$.¹¹ The equation of state of D. Berthelot seems, however, to be particularly adapted to such calculations,¹² except at very low temperatures.¹³

An apparatus for the measurement of the velocity of sound in small quantities of gas at different temperatures is described.¹⁴

Molecular Structure.

Several calculations of molecular diameters from the viscosities of gases have been made.¹⁵ In size and shape the atoms of monatomic inert elements are nearly indistinguishable from the atoms, respectively, of the neighbouring diatomic elements in the periodic table, the dimensions of which have been deduced indirectly from X-ray crystal measurements. A chlorine molecule may be regarded as having the size and shape of two argon atoms in contact, that is, with their external electron shells touching each other. Gaseous bromine is similarly related to double krypton atoms, and iodine to xenon. An oxygen molecule has the same size and shape as two neon atoms in contact. The shape of a molecule composed of

⁶ F. Skaupy, *Z. Physik*, 1921, **4**, 100; *A.*, ii, 300.

⁷ Paul Günther, *Ann. Physik*, 1920, [iv], **63**, 476; *A.*, ii, 16.

⁸ *A.*, 1912, ii, 1134.

⁹ H. B. Dixon, C. Campbell, and A. Parker, *Proc. Roy. Soc.*, 1921, [A], **103**, 1; *A.*, ii, 621.

¹⁰ W. Herz, *Z. Elektrochem.*, 1921, **27**, 125; *A.*, ii, 299.

¹¹ *A.*, 1919, ii, 494.

¹² Compare W. Rücker, *Ann. Physik*, 1921, **65**, 393.

¹³ Schimank, *Physik. Z.*, 1916, **17**, 393.

¹⁴ F. Himstedt and R. Widder, *Z. Physik*, 1921, **4**, 355.

¹⁵ A. O. Rankine, *Proc. Roy. Soc.*, 1921, [A], **98**, 360, 369, 331; *A.*, ii, 192, 192, 489; compare *Phil. Mag.*, 1921, [vi], **42**, 615.

two equal atoms is assumed to be a spheroid, the volume of which is equal to the sum of the volumes of the hard elastic spheres to which each participating atom is equivalent. The nitrogen molecule is equivalent to a hard, elastic body nearly spherical in shape. The close similarity between the physical properties of nitrous oxide and carbon dioxide again appears from viscosity measurements: their molecules appear to have the same size and shape, and possess an external electron arrangement practically the same as that of three neon atoms in line and contiguous. The diameter of the outer electron shell of cyanogen is nearly equal to that of bromine, as found from crystal measurements. This agrees with the equality of the molecular volumes of potassium bromide and cyanide, and with the assumptions of Lewis¹⁶ and Langmuir¹⁷ with regard to the similarity of the nitrogen and cyanogen molecules. Non-spherical molecules, built up of atoms of unequal sizes, have also been considered.¹⁸ The increases in diameter in passing from neon to ammonia, argon to phosphine, and krypton to arsine are approximately equal, and may represent the effect of the addition of the three nuclei of the hydrogen atoms added to complete the electron configuration of the corresponding inert atom. The calculations are based on Chapman's modification of Sutherland's formula: $4\pi\sigma^2 = 0.491(1 + \epsilon)\rho\bar{V}/\sqrt{2v\eta}(1 + C/T)$, where σ = radius of molecule; ρ = density; \bar{V} = mean speed; v = no. of molecules per c.c., η = viscosity, ϵ is practically = 0, C is a constant, T = abs. temperature.

The symmetrical shapes of polyatomic molecules assumed in such calculations as the above introduce difficulties in other departments of physical measurement, particularly in connexion with the molecular heats. This matter has been discussed¹⁹ and the formulæ of water, hydrogen sulphide, and ammonia deduced from the theory of Lewis¹⁶ assuming distortion of the octets. In water, the linking angle is approximately the same as that between carbon bonds. The distance between the oxygen nucleus and the hydrogen nuclei is the same in both cases, but is different from that between the two hydrogen nuclei. The two hydrogen atoms lie in one half of the resulting tetrahedron and two electron pairs in the other half, expressing the dipolar character of water. An asymmetric structure favours association.

The structure of molecules has also been considered²⁰ on the

¹⁶ *A.*, 1916, ii, 310.

¹⁷ *Ibid.*, 1919, ii, 328.

¹⁸ A. O. Rankine, *Proc. Physical Soc.*, 1921, **33**, 362; *A.*, ii, 584; *Phil. Mag.*, 1921, [vi], **42**, 601.

¹⁹ E. J. Cuy, *Z. Elektrochem.*, 1921, **27**, 371; *A.*, ii, 584.

²⁰ G. Kirsch, *Z. physikal. Chem.*, 1920, **96**, 471; *A.*, ii, 193.

basis of Kossel's hypothesis.²¹ The stability of the nitrogen molecule is due to the additional nucleus, and the similarity of the $-\text{CN}$ group to halogens (see above) is due to this cause. Similar stabilising nuclei are assumed to be present in the molecules of carbon monoxide, ozone, oxides of nitrogen, and the $-\text{CNO}$ radicle.

The cubical atom theory has been considered²² from the point of view of internal structure, and the radii of atoms have been calculated. The electronic affinities and heats of formation can also be satisfactorily found.²³

The collision between molecules and free electrons has been studied.²⁴ In the case of slow electrons (1 volt) it was found that the electron is either absorbed outright, or not in any way influenced as regards its direction and velocity by the gas molecule. For every atom or molecule there seems to be a fixed sphere of action, outside which a slow electron is not influenced, but inside which it is strongly influenced. A law of force of rapidly diminishing *continuous* distance action is regarded as improbable. Argon shows deviations, and is also peculiar in exhibiting selective absorption.

Molecular volumes have been considered²⁵ from the point of view of the Lewis-Langmuir theory, and particularly the theory of isosteres. Isosteric molecules and nuclear atoms in hydrogen compounds are shown to have the same volume. The latter depends on the number and arrangement of the electrons surrounding the nucleus rather than on the charge on the latter. Nitrogen and carbon monoxide molecules probably have a normal acetylenic structure, three pairs of electrons being shared, rather than the condensed structure suggested by Langmuir (see above).

An interesting theory of colour in relation to molecular structure has been put forward.²⁶ In some cases, an atom of large atomic volume is unable to form a stable octet by taking an electron from an atom of small atomic volume, in which the attraction between the kernel and electrons is greater. An unstable orbit, which may be disturbed by light, then results. It has been known for some time that compounds in which an atom is unsaturated, or in which

²¹ *A.*, 1916, ii, 243.

²² A. Landé, *Z. Physik*, 1920, **2**, 87; *A.*, ii, 189; *ibid.*, 380; *A.*, ii, 189; E. Madelung and A. Landé, *ibid.*, 230; *A.*, ii, 190; H. Schwendenwein, *ibid.*, 1921, **4**, 73; *A.*, ii, 310.

²³ See *Ann. Reports*, 1920.

²⁴ H. F. Mayer, *Ann. Physik*, 1921, [iv], **64**, 451; *A.*, ii, 234; C. Ramsauer, *ibid.*, 513; *A.*, ii, 324; O. Klein and S. Rosseland, *Z. Physik*, 1921, **4**, 46; *A.*, ii, 291.

²⁵ R. N. Pease, *J. Amer. Chem. Soc.*, 1921, **43**, 991; *A.*, ii, 437.

²⁶ J. Meisenheimer, *Z. physikal. Chem.*, 1921, **98**, 304; *A.*, ii, 364.

two atoms of the same element exhibit different valencies, are usually coloured.

When the atomic diameter is calculated from b of van der Waals's equation by the formula $\sigma = (3b/2\pi N)^{\frac{1}{3}}$, where $N = 2.75 \times 10^{19}$, the increase in passing from one inert gas to another is constant (0.28×10^{-8} cm.). This relation is not obtained when σ is calculated from the viscosities; it is in agreement with Langmuir's theory.²⁷ The atomic radii of helium, neon, argon, krypton, and xenon are supposed, on the basis of theoretical considerations,²⁸ to be in the proportion 3 : 4 : 6 : 7 : 8. The true radii of the atoms are multiples of one "elementary length," 0.036 to 0.039 Å.

An ingenious calculation of the absorption spectrum of hydrogen chloride from the quantum theory of molecular rotations²⁹ lends support to the existence of the two isotopes of chlorine.

Surface Tension.

Further investigations of thin films on water have been made.³⁰ Any further quantity of oleic acid, placed on water already covered with a layer of thickness double that which corresponds with the maximum extension, does not undergo spontaneous extension, but forms globules. The layer is then regarded as "saturated." If the surface occupied by a given quantity of oleic acid is reduced, the tension decreases and then suddenly becomes constant. An improved technique for the investigation of thin films on water has been described.³¹ The compressibility curves of the film are accurately straight lines, with a doubtful deviation at very low compressions. An abrupt change in the properties of the film takes place at an acidity of $10^{-5}N$, under compression less than 16 dynes/cm. The area occupied by each molecule becomes about 20 per cent. greater than on neutral solutions. Langmuir's view³² that the films consist of a single layer of molecules, with the carboxyl groups turned towards the water, is confirmed and extended. Different films, and even different parts of the same

²⁷ L. St. C. Broughall, *Phil. Mag.*, 1921, [vi], **41**, 872; *A.*, ii, 445.

²⁸ M. Pierucci, *Nuovo Cim.*, 1921, [vi], **22**, 189; *A.*, ii, 583; compare *A.*, 1920, ii, 538.

²⁹ A. Kratzer, *Z. Physik*, 1920, **3**, 460; *A.*, ii, 140; *ibid.*, 289; *A.*, ii, 142. Compare W. L. Bragg and H. Bell, *Nature*, March 24, 1921; *A.*, ii, 689; G. Hettner, *Z. Physik*, 1920, **1**, 345; *A.*, ii, 144; E. S. Imes, *Astrophys. J.*, 1919, **50**, 251; *A.*, ii, 4; A. Haas, *Z. Physik*, 1921, **4**, 68; *A.*, ii, 286; F. W. Loomis, *Astrophys. J.*, 1920, **52**, 248; *A.*, ii, 530.

³⁰ A. Marcein, *Compt. rend.*, 1921, **173**, 38; *A.*, ii, 488. Compare *Ann. Physique*, 1913.

³¹ N. K. Adam, *Proc. Roy. Soc.*, 1921, [A], **99**, 336; *A.*, ii, 488.

³² *A.*, 1917, ii, 525.

film, vary considerably in their resistance to collapse on compression. The latter seems to be aided by nuclei. A mutual influence between saturated and unsaturated molecules in the same film has been detected.³³

The adhesional work, W_A , between mercury and organic liquids has been calculated³⁴ by the formula $W_A = \gamma_1 + \gamma_2 - \gamma_{12}$, where γ_1 and γ_2 are the free surface energies of the two liquids and γ_{12} the free surface energy of the interface. In some cases the latter is negative,³⁵ and the surfaces rise in temperature when they are formed. The liquids which show this abnormal behaviour in contact with water are heptinene, *n*- and *sec.*-octyl alcohols, and heptaldehyde. Addition of oxygen increases the tensile energy feebly, whilst the adhesional energy towards water is largely increased. Double bonds show the opposite effects. The facts are explained on the assumption that unsymmetrical molecules are oriented in the surface. Oxygen atoms turn towards the water. The length of a hydrocarbon chain is of more importance in determining the solubility than the nature of the active group at the end of the molecule. The triple bond has a greater relative effect on the adhesional energy than on the adhesional work at 20° as compared with a hydroxyl oxygen atom.

The surface tension of mercury in a vacuum at various temperatures has been determined by the drop method^{36, 37} and the interfacial tensions between mercury and a number of organic liquids have been found by the same method. The adhesional work between mercury and an organic liquid is always greater than between water and the liquid, or between the liquid and itself. It decreases rapidly with increase of temperature, whilst the total energy increases.

The statical measurement of interfacial tension, and the relation between interfacial tension and surface tension in organic solvents in contact with aqueous solutions have been described.³⁸

By combining Trouton's rule with the Eötvös expression, the relation $L = 20\gamma/S^3M^{\frac{2}{3}}$, where L = latent heat, M = molecular weight, γ = surface tension at the boiling point and S = density at the boiling point, has been deduced.³⁹ This holds approximately

³³ P. Woog, *Compt. rend.*, 1921, **173**, 387; *A.*, ii, 575.

³⁴ W. D. Harkins and E. H. Grafton, *J. Amer. Chem. Soc.*, 1920, **42**, 2534; *A.*, ii, 87.

³⁵ W. D. Harkins and Y. C. Cheng, *ibid.*, 1921, **43**, 35; *A.*, ii, 242; compare *A.*, 1920, ii, 357.

³⁶ W. D. Harkins and W. W. Ewing, *ibid.*, 1920, **42**, 2539; *A.*, ii, 87.

³⁷ J. Palacios, *Anal. Fis. Quím.*, 1920, **18**, 294; *A.*, ii, 304.

³⁸ W. C. Reynolds, *T.*, 1921, **119**, 460, 466.

³⁹ W. Herz, *Z. Elektrochem.*, 1921, **27**, 25; *A.*, ii, 300.

for normal, but not for associated, liquids. From this the molecular diameter d may be calculated by the formula $d = 1/10(M/S)^{\frac{1}{3}} \cdot 0.00102/42700$. The internal pressure is calculated by the formula $B = L/2v = 10\gamma/(Mv)^{\frac{1}{3}} \times 42700/1033$, where Mv is the molecular volume. The following values were found: benzene 1830 atm., ethyl acetate 1425 atm., aniline 2120 atm.

The latent heat may also be calculated from the critical data by the equation $L = 0.00093T_s/d_c v_c$, where T_s is the absolute boiling point, and d_c and v_c are the critical density and volume, respectively.⁴⁰ From the Trouton rule it follows that $M \times 0.00093/d_c v_c$ must be constant. This is approximately the case with normal liquids.

It has been shown⁴¹ that if the glass is properly cleaned, and evaporation of liquid prevented, the supposed finite contact angle in the measurement of the surface tensions of some organic liquids does not exist. The correction for the capillary rise in wide tubes calculated by Laplace and Rayleigh was also verified.⁴²

The effect of adsorbed gases on the surface tension of water has been found; the surface tension is diminished by an amount which is greater the higher the density of the gas, except for carbon dioxide.⁴³

The relation $1/\beta J = -2\lambda_1 s$, in which λ_1 is the internal latent heat, β the compressibility, and s the specific gravity, of a liquid, has been deduced⁴⁴ from van der Waals's equation on the assumption that a is independent of volume. If a depends on volume, $1/\beta J = \epsilon \lambda_1 s$, where $\epsilon = \rho/\alpha$ and $\rho = 1/\sigma \cdot \partial\sigma/\partial T$, the coefficient of variation of surface energy σ with temperature; $\alpha = 1/v \cdot \partial v/\partial T$. The first equation is approached at higher temperatures, the second at lower temperatures. J is the mechanical equivalent of heat.

The equation $MLJ = \pi\gamma d^2 N + RT$, where d is the molecular diameter, γ the surface tension, and N Avogadro's number, has been deduced⁴⁵ for the latent heat of evaporation. The values of d calculated agree with those found by Bragg, or from kinetic theory. Vaporisation is considered as a discontinuous change, the elementary quantity of energy concerned being $10 \times 10^{-16}T$ ergs. The value of K in $\pi\gamma d^2 N = K(T_c - T)$ agrees with that from Eötvös's law. The connexion between Trouton's rule and Wien's

⁴⁰ W. Herz, *Z. Elektrochem.*, 1921, **27**, 26; *A.*, ii, 300; compare *A.*, 1919, ii, 494.

⁴¹ T. W. Richards and E. C. Carver, *J. Amer. Chem. Soc.*, 1921, **43**, 827; *A.*, ii, 384; compare *A.*, 1915, ii, 522.

⁴² Compare also S. Sugden, *T.*, 1921, **119**, 1483.

⁴³ S. S. Bhatnagar, *J. Physical Chem.*, 1920, **24**, 716; *A.*, ii, 169; compare also reference ⁴¹.

⁴⁴ D. L. Hammick, *Phil. Mag.*, 1921, [vi], **41**, 21; *A.*, ii, 84; compare Lewis, *Z. physikal. Chem.*, 1911, **78**, 24.

⁴⁵ R. Audubert, *Compt. rend.*, 1921, **172**, 375; *A.*, ii, 240.

displacement law, $\lambda_m T = \text{const.}$, has also been pointed out.⁴⁶ The latent heat of evaporation is given by $L = N h \nu$, where h is Planck's constant, and ν a frequency, but the critical energy increment is an average value. The formula is obtained as follows: $\lambda_m T_c = 0.28986$; $\nu = c/\lambda_m$ ($c =$ velocity of light); hence $L = N h \nu = N h c T_c / 0.28986 = 9.866 T_c$.

The latent heats of fusion per gram-atom of the inactive gases have been calculated.⁴⁷ The value of Eucken's measurement⁴⁸ of the latent heat of fusion of argon, 0.268 kg.cal., is used. The following values were found: helium < 0.004; neon, 0.08; krypton, 0.33; xenon, 0.43; niton, 0.65.

Properties of Liquids; Association.

The constants a and b of van der Waals's equation may be calculated, in the case of normal liquids, from the number of atoms in the molecule, n ; the number of valencies in the molecule, z ; the critical data, and other constants.⁴⁹ The following equations were deduced for the constant b : $b = 412n10^{-6} = 201z10^{-6} = 795.16 \times M^2 10^{-4} / T_c^2 d_s = 12354 d_s 10^{-3} / p_c^2$. The constant a is calculated from the equations: $a = 5.094n T_c 10^{-6} = 2.49z T_c 10^{-6} = 4.5846n^2 p_c 10^{-6} = 1474.713 M^2 10^{-6} / T_s d_s = 23992 d_s T_s 10^{-6} / p_c^2$. The coefficient of expansion of normal liquids may be calculated from a and b .

The "constant" a in Thorpe and Rucker's formula for the dependence of specific volume on temperature: ⁵⁰ $V_0/V_t = (aT_c - T)/(aT_c - 273)$ is shown to decrease with increasing temperature.⁵¹ In most series of analogous substances, a increases with the molecular weight; with the exception of the value for water it lies between 1.5 and 2.1.

In the case of organic liquids containing carbon, hydrogen, and oxygen, the relation $n = 193M^2/T_s^2 d_s$ has been deduced by Groshans. If this is combined with the relation $n = 1.1T_c/p_c$ and with Trouton's rule, it follows⁵² that $M/T_s^2 = 0.00077$. This holds with approximate accuracy for compounds ranging from ethane ($T_s = 187.6$) to anthraquinone ($T_s = 653$). By combining Groshans's equation with the relation $v_c = 0.0009n$, it is shown that $v_c = 0.1737M^2/T_s^2 d_s$, or from the above equation, $v_c = 1.34 \times 10^{-4} M/d_s$. The values of

⁴⁶ E. K. Rideal, *Phil. Mag.*, 1921, [vi], **42**, 156; *A.*, ii, 489.

⁴⁷ J. Narbutt, *Physikal. Z.*, 1921, **22**, 52; *A.*, ii, 163.

⁴⁸ Eucken, *Beibl. Ann. Phys.*, 1916, **40**, 322.

⁴⁹ W. Herz, *Z. Elektrochem.*, 1921, **27**, 373; *A.*, ii, 573.

⁵⁰ *T.*, 1884, **45**, 135.

⁵¹ W. Herz, *Z. physikal. Chem.*, 1921, **97**, 376; *A.*, ii, 374.

⁵² W. Herz, *Z. anorg. Chem.*, 1921, **116**, 250; *A.*, ii, 484; compare Jorissen, *A.*, 1920, ii, 90; *A.*, ii, 484; compare also *A.*, 1920, ii, 285.

v_c calculated for a number of esters of fatty acids agree well with those observed. The relation between specific heat s and critical data for the higher paraffins can be expressed by $sM = 2.44T_c/p_c$.

The ratio of molecular volume to density is not constant at corresponding temperatures for normal and associated liquids.⁵³ The ratio d_s/d_c , where d_s and d_c are the densities at the boiling point and at the critical temperature, is 2.69 for monohalogenated benzenes. The assumption of constancy of the ratio of molecular volume to density would give $M_c/M_s = 2.69d_c/d_s$, where M_c and M_s are the molecular weights at the critical temperature and the boiling point. For a number of known associated liquids the ratio was found to be nearly unity. It is concluded that the theory of corresponding states cannot be applied where changes of molecular state occur.

The ratio of the densities of liquid and vapour has been shown to be a function of the reduced temperature T/T_c , and as a first approximation does not depend on the individual properties of the liquid.⁵⁴ The value of B in the equation $B = d_l^2/T \log K$, where d_l = density of liquid and $K = d_l/d_v$ is the ratio just referred to, is found to be practically constant for normal liquids. It shows a slight maximum at the point $T/T_c = 0.60$ to 0.65 and a slight minimum at the point $T/T_c = 0.85$ to 0.90 . In the case of associated liquids, the value of B increases with temperature and exhibits no maximum or minimum.

The equation of Mendeléev: $D_t = D_0(1 - Kt)$, where D_0 and D_t are the densities of a liquid at 0° and t° , and K is a constant, has been tested with benzene, its halogen substitution products, and mixtures of these.⁵⁵ It represents the facts equally for normal and for associated liquids, within the limits of experimental error, and cannot be used to differentiate between the two groups. The constant K for mixtures can probably be calculated by the mixture rule.

Hydrogen has been found to obey the law of rectilinear diameter.⁵⁶ The critical density is calculated as 0.03 at -239.91° .

A relation between the critical data and the chemical constant has been deduced.⁵⁷ The chemical constant is calculated by the equation $C = \lambda_0/4.571T$, where $\lambda = (\lambda_0 + AT - BT^2 - \dots)$

⁵³ W. Herz, *Z. anorg. Chem.*, 1921, **115**, 237; *A.*, ii, 436.

⁵⁴ W. Swientoslawski, *Bull. Soc. chim.*, 1921, [iv], **29**, 499; *A.*, ii, 535; *ibid.*, 507; *A.*, ii, 536.

⁵⁵ W. Herz and J. Meyer, *Z. physikal. Chem.*, 1921, **97**, 381; *A.*, ii, 381.

⁵⁶ E. Mathias, C. A. Crommelin, and H. K. Onnes, *Compt. rend.*, 1921, **172**, 261; *A.*, ii, 256.

⁵⁷ Fr. A. Henglein, *Z. anorg. Chem.*, 1920, **114**, 234; *A.*, ii, 163; *Z. physikal. Chem.*, 1921, **98**, 1.

$(1 - p/p_k)$ is the latent heat and p_k, T_k are the critical constants. Nernst's equation, $C = 0.14\lambda/T_B$, where T_B is the absolute boiling point, follows from van der Waals's equation, $\log p/p_k = a(1 - T_k/T)$. Cederberg's equation, $C = k \log p_k$ (where k is 1.6 in many cases), also follows from this equation, since it is a special case of the more general equation, $C = 1.1 \log p_k/(T_k/T_B - 1)$.

The critical temperature of mercury has been calculated,⁵⁸ from the change of surface tension with temperature, as 1474°. Another calculation⁵⁹ from theoretical considerations gave 1700°, the critical pressure being estimated at 1100 atm.

If in van der Waals's vapour pressure equation the critical temperature is replaced by the expression $\frac{1}{2}(1/K_{20} + 293)$, where K_{20} is the coefficient of expansion at 20°, the value of the constant a is close to, generally greater than, 3 for a number of esters. The critical pressure p_c in the same equation can be replaced by $1/K_{20} + 293/0.88n$, where n is the sum of the valencies of the constituent atoms. The constant in Cederberg's formula (see above) has an abnormally high value for organic compounds, increasing with the molecular weight.⁶⁰

The equation $p = RT(d_1 + d_2)(d_2/d_1)^{(d_1 + d_2)/(d_1 - d_2)}$, where p is the vapour pressure, and d_1 and d_2 are the densities of liquid and vapour, has been deduced.⁶¹ The quantity $d_1 + d_2$ may be regarded as a density factor which is a measure of the cohesive forces per unit mass.

Radiation and the Quantum Theory.

The interpretation of the chemical constant, as given by Nernst and by Sackur, has been criticised.⁶² The chemical constants of zinc (1.62) and cadmium (1.56) have been calculated⁶³ by Nernst's formula. These differ somewhat from the values obtained by Egerton,⁶⁴ from whose results they are deduced, but agree with the value 1.59 given by the Sackur-Stern-Tetrode formula. The theory of the chemical constant, from the point of view of statistical mechanics, has been considered,⁶⁵ and the quantum theory has been applied to the theory of corresponding states.⁶⁶ An expression is

⁵⁸ G. Meyer, *Physikal. Z.*, 1921, **33**, 76; *A.*, ii, 238.

⁵⁹ J. J. van Laar, *Proc. K. Akad. Wetensch. Amsterdam*, 1920, **23**, 267, 282; *J. Chim. Phys.*, 1920, **18**, 273; *A.*, ii, 83.

⁶⁰ W. Herz, *Z. Elektrochem.*, 1921, **27**, 125; *A.*, ii, 302.

⁶¹ J. H. Shaxby, *Phil. Mag.*, 1921, [vi], **41**, 441; *A.*, ii, 239.

⁶² E. Yamazaki, *J. Tokyo Chem. Soc.*, 1920, **41**, 19; *A.*, ii, 574.

⁶³ G. Heidhausen, *Z. Elektrochem.*, 1921, **27**, 69; *A.*, ii, 240.

⁶⁴ *A.*, 1920, ii, 84.

⁶⁵ W. Schottky, *Physikal. Z.*, 1921, **22**, 1; *A.*, ii, 179.

⁶⁶ A. Byk, *ibid.*, 15; *A.*, ii, 163.

obtained which represents the physical properties of the liquid state, and covers the abnormalities observed with substances of small molecular weight.

In the application of the quantum theory to evaporation,⁶⁷ two formulæ may be used: (1) $L = Nh(v_2 - v_1)$, where v_1 and v_2 are the frequencies of the solid or liquid and of the vapour, respectively; (2) $L = \frac{1}{2}Nh \{v_5 - (v_3 + v_4)\}$ where v_3 , v_4 , and v_5 are the frequencies of activation of the positive nucleus, of the electron, and the radiation frequency, respectively.

On the basis of the similarity between evaporation and solution, it has been suggested⁶⁸ that Trouton's rule should have an analogue in solution, $\lambda/T = \text{const.}$, where λ is the molecular heat of solution and T the temperature which corresponds, for a state of saturation, with an osmotic pressure of 1 atm. By extrapolation from the results with a number of salts, the value was found to be 30—32. From this the elementary quantity of energy involved when a molecule passes into solution was calculated as $18 \times 10^{-16} \cdot T$ ergs, which is the same as that found for the energy of dissociation of solids and of sublimation.

The applications of statistical methods to chemical equilibria have been reported.⁶⁹ The theory of the velocity of unimolecular reactions from the point of view of the radiation hypothesis has been critically discussed.⁷⁰ It is concluded that the similarity in form between the Arrhenius formula, giving the dependence of reaction velocity on temperature, and Wien's law, for the intensity of radiation as a function of temperature, is purely accidental. The absence of absorption bands where they would be indicated by the hypothesis of activating frequencies, and the fact that the energy available, in the form of radiation, is very much less than required, are urged against the hypothesis. A modification of the radiation hypothesis has been proposed⁷¹ which meets some of the objections. The dependence of the unimolecular reaction constant on temperature can be fairly satisfactorily represented by the expression $k = se^{-Q/RT}$, but the significance of s and Q have been differently interpreted.⁷² It is suggested that Q represents the difference between the energy of the reacting molecules and the *average* energy of all the molecules of that kind. The

⁶⁷ E. K. Rideal, *Proc. Camb. Phil. Soc.*, 1921, **20**, 291; *A.*, ii, 431.

⁶⁸ R. Audubert, *Compt. rend.*, 1921, **172**, 676; *A.*, ii, 303.

⁶⁹ K. F. Herzfeld, *Physikal. Z.*, 1921, **22**, 186; *A.*, ii, 313.

⁷⁰ I. Langmuir, *J. Amer. Chem. Soc.*, 1920, **42**, 2190; *A.*, ii, 31; compare also M. Polányi, *Z. Physik*, 1920, **3**, 31; *A.*, ii, 179.

⁷¹ R. C. Tolman, *J. Amer. Chem. Soc.*, 1921, **43**, 269; *A.*, ii, 248.

⁷² Compare W. C. McC. Lewis, *T.*, 1918, **113**, 471; Lewis and A. McKeown, *J. Amer. Chem. Soc.*, 1921, **43**, 1288; *A.*, ii, 623.

theoretical conclusions are confirmed by an investigation⁷³ of the photochemical decomposition of nitrogen pentoxide. The frequency corresponding with the critical increment may be calculated from the effect of temperature on the reaction velocity according to the equations: $d \log_e K/dT = E/RT^2$ and $E = Nh\nu$,⁷⁴ but light of this frequency is found not to decompose nitrogen pentoxide. In presence of nitrogen dioxide, however, light of 400—460 $\mu\mu$ accelerates the decomposition of the pentoxide, but this does not take place without the dioxide, or in the dark in presence of dioxide. It is suggested that the nitrogen dioxide acts as a photo-catalyst by absorbing radiation, transforming it through fluorescence and giving it out at a particular frequency which is effective in bringing about the decomposition of the pentoxide. The experimental verification of this hypothesis would certainly lend valuable support to the radiation theory of catalysis.

The quantum theory of chemical reaction leads to the equation $k_1 = \nu e^{-Q/RT}$ for the velocity constant of a unimolecular reaction,⁷⁵ where ν is a frequency and Q the heat of activation. It is assumed that $Q = Nh\nu$, which agrees with the experimental results on the decomposition of phosphine. For bimolecular reactions the equation:

$$k_2 = N\sigma^2\sqrt{8\pi RT}(1/M_A + 1/M_B)e^{-\frac{Q_A + Q_B}{RT}}$$

is deduced, where σ is the mean molecular diameter, M_A and M_B the molecular weights, of A and B , and $Q_A + Q_B$ the total heat of activation. This agrees with experiment. Investigation of the influence of the solvent on the temperature coefficient of reaction velocity has been found,⁷⁶ in the case of similar solvents, in some sense to support the deduction from the radiation hypothesis that there is an inverse proportionality between velocity and temperature coefficient. This does not hold for dissimilar solvents. These are not regarded as simple catalysts, and "the radiation theory does not apply to such cases." Tolman's criticisms of Marcelin's deduction of the equation for reaction velocity (see above) has been examined⁷⁷ and its validity questioned.

Einstein's photochemical equivalence law, $n = Q/h\nu$, where n = no. of molecules decomposed, Q = energy absorbed, ν = fre-

⁷³ F. Daniels and E. H. Johnston, *J. Amer. Chem. Soc.*, 1921, **43**, 53, 72; *A.*, ii, 249. Compare E. C. C. Baly and W. F. Barker, *T.*, 1921, **119**, 662.

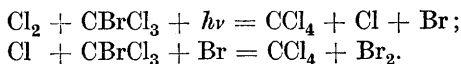
⁷⁴ J. Perrin, *A.*, 1919, ii, 177; W. C. McC. Lewis, *T.*, 1918, **113**, 471.

⁷⁵ S. Dushman, *J. Amer. Chem. Soc.*, 1921, **43**, 397; *A.*, ii, 315.

⁷⁶ H. E. Cox, *T.*, 1921, **119**, 142.

⁷⁷ E. P. Adams, *J. Amer. Chem. Soc.*, 1921, **43**, 1251; *A.*, ii, 628.

quency, has been confirmed ⁷⁸ for the reactions between bromine and *cyclohexane* (gaseous) and chlorine and trichlorobromomethane (liquid). The latter was found to be a good "acceptor" for activated chlorine molecules. A solution of chlorine in the liquid on exposure to light probably undergoes the following reactions:



The bromine could be determined spectrophotometrically; the radiation absorbed was determined by a thermopile as usual. The phenomena are explained on Bohr's theory as follows: a quantum $h\nu$ is absorbed by the chlorine molecule, the valency-electron springs to a larger ring, and the molecule is activated. This active state has a given "life" (calculated as 10^{-10} secs.), during which it may react with an acceptor. If no acceptor is present, the activated molecule gives up energy in the form of other quanta (luminescence, or heat), or transfers it to indifferent molecules, causing a general rise of temperature.

Physical Properties and Chemical Composition.

Some empirical relations between the absolute critical temperature, boiling point, and melting point ⁷⁹ have been shown ⁸⁰ to be purely arithmetical and to have no physical meaning. New relations are deduced from van der Waals's formula $\log p/p_c = f(T_c/T - 1)$, where f may depend slightly on the temperature. If $T_1 =$ boiling point, $p = 1$ atm., then $\phi_1 = T_c/T = \log p_c/f + 1$. ϕ_1 will therefore be approximately constant unless p_c is abnormal (helium). In the case of fusion, $(v_2 - b_2)/v_2 = 1/14$, where $v_2 - b_2$ is the effective volume for molecular motion. Thence $\phi_2 = T_c/T_2 = 2a_c/\gamma a_2$, where $T_2 =$ m. p., $a =$ attraction constant, γ is usually 0.9 but for ideal substances (a and b constant) is 0.5. For ordinary substances, $a_2 = 1.4a_c$; $\phi_2 = 2$. For limiting substances (with T_c from 400° to 500°), $\phi_2 = 1.83$, which agrees with the rule of Timmermans ⁸¹ that the melting points of different families of substances tend to an upper limit of 117° .

The cause of the alternate higher and lower melting points of successive members of the fatty acid series has been explained ⁸²

⁷⁸ W. Noddack, *Z. Elektrochem.*, 1921, **27**, 359; *A.*, ii, 568; see also E. C. C. Baly and W. F. Barker, *T.*, 1921, **119**, 653, for a study of the reaction $\text{H}_2 + \text{Cl}_2 = 2\text{HCl}$.

⁷⁹ M. Prud'homme, *J. Chim. phys.*, 1920, **18**, 270, 307, 359; *A.*, ii, 83, 84, 376.

⁸⁰ J. J. van Laar, *J. Chim. phys.*, 1921, **19**, 4; *A.*, ii, 622.

⁸¹ *A.*, ii, 430.

⁸² G. Tammann, *Z. anorg. Chem.*, 1919, **109**, 221; *A.*, 1920, ii, 285.

on the hypothesis that acids with an even number of carbon atoms exist in two stable crystalline forms. In support of this, it was shown that acetic acid exists in two forms with a triple point at 57.5° at 2330 kilos. per sq. cm. No isomerism was found with formic acid. Attention is now⁸³ directed to the obvious insecurity in basing such a general theory on two observations. It is shown that many other physical properties show the same kind of alternation in homologous series. When the numerical value of the property (solubility, molecular rotation, boiling point) is plotted against the number of carbon atoms, the points corresponding with an even number of carbon atoms lie on one smooth curve, and those corresponding with an odd number on another. These regularities may be explained on the hypothesis⁸⁴ of the alternate positive and negative character of carbon atoms in a chain. The theory of isomerism, however, is obviously still open to experimental confirmation.⁸⁵

The relation between heats of combustion and constitution has been discussed.⁸⁶ Symmetrical nitro-compounds appear to be most stable.

Guldberg's rule, that the (absolute) boiling point at 1 atm. is equal to two-thirds of the critical temperature, is approximately correct. Atmospheric pressure, however, is not a constant fraction of the critical pressure, and an attempt has been made⁸⁷ to test the relationship at fractions $\frac{1}{33}$ and $\frac{1}{50}$ of the critical pressure. With organic liquids $\frac{1}{50}$ gave better results, but with inorganic liquids (water, nitrogen, hydrogen sulphide) the constant was lower than with organic liquids.

A linear relation $y = \alpha x + a$ has been found⁸⁸ to hold between the molecular volume y of one haloid salt and the corresponding volume x of another haloid, the two salts containing a common kation or anion. The question is raised whether the crystalline structure of cæsium haloids is the same as that of the other alkali haloids. The distance between oppositely charged ions in haloid salts is calculated as $r = 0.938 \times 10^{-8} \sqrt[3]{V}$ cm., where V is the molecular volume of the salt.

⁸³ E. J. Cuy, *Z. anorg. Chem.*, 1921, **115**, 273; *A.*, ii, 429.

⁸⁴ *Idem.*, *J. Amer. Chem. Soc.*, 1920, **42**, 503; *A.*, 1920, i, 361. Compare A. Lapworth, *Mem. Manchester Phil. Soc.*, 1920, **64**, (iii), 1; *A.*, ii, 543; M. T. Hanke and K. K. Koessler, *J. Amer. Chem. Soc.*, 1918, **40**, 1726; *A.*, 1919, i, 4.

⁸⁵ Compare Tammann, *Z. anorg. Chem.*, 1921, **115**, 288; *A.*, ii, 430.

⁸⁶ O. H. Binder, *Chem. Zeit.*, 1921, **45**, 477; *A.*, ii, 435; W. E. Garner and C. L. Abernethy, *Proc. Roy. Soc.*, 1921, [A], **99**, 213; *A.*, ii, 435; compare *T.*, 1921, **119**, 6.

⁸⁷ R. Lorenz and W. Herz, *Z. anorg. Chem.*, 1921, **115**, 100; *A.*, ii, 433.

⁸⁸ K. Fajans and H. Grimm, *Z. Physik*, 1920, **2**, 299; *A.*, ii, 168.

Theory of Mixtures.

The vapour pressures of liquid mixtures have been considered⁸⁹ from the thermodynamic point of view, and it is shown that the assumption of chemical combination is unnecessary in many cases to explain the results. Evidence of chemical combination was found with sulphuric acid and ethyl ether.

The thermodynamic theory of mixtures,⁹⁰ and the theory of Dolezalek⁹¹ have also been further discussed. An attempt has been made⁹² to apply the latter theory to the electromotive behaviour of alloys.

Electrolytic Conductivity ; Ionisation.

The abnormality of strong electrolytes has been further considered. On the assumption that interionic forces in solution are inverse square functions of the distances apart of dissimilar ions, and that the forces causing dissociation are inverse higher power functions of the distances between molecules, an interpretation of some types of dilution law is obtained.⁹³ Complete ionisation is not assumed, and the law of mass action holds good if active mass is represented by a momentum term. The assumption that the abnormality is due to the abnormal osmotic behaviour of the ions is in entire agreement with the fundamental assumptions made.

The theory of Ghosh⁹⁴ has been further criticised. It is shown⁹⁵ that in his calculation of the number of ions having kinetic energies in excess of a given value ("free ions"), Ghosh has used an incorrect formula. When the correct expression is used, the results are no longer in good agreement with experiment.

The dielectric constants of some electrolytic solutions have been determined.⁹⁶ The electrolytes lowered the dielectric constant of water in a way similar to that of the majority of non-electrolytes.

The limiting value of the molecular conductivity, λ_{∞} , in non-

⁸⁹ A. W. Porter, *Trans. Faraday Soc.*, 1921, **16**, 336; *A.*, ii, 377.

⁹⁰ M. B. Wagner, *Z. physikal. Chem.*, 1920, **96**, 287; 1921, **97**, 229, 330, 337, 343; *A.*, ii, 162, 300, 375; compare *A.*, 1920, ii, 596, 597.

⁹¹ *A.*, 1909, ii, 22; 1913, ii, 482; H. Cassel, *Z. Physik*, 1920, **2**, 146; *A.*, ii, 166; A. Schulze, *Z. physikal. Chem.*, 1921, **97**, 388, 417; *A.*, ii, 388, 390.

⁹² F. Clotofski, *Z. anorg. Chem.*, 1920, **114**, 1; *A.*, ii, 203.

⁹³ W. Hughes, *Phil. Mag.*, 1921, [vi], **42**, 134, 428; *A.*, ii, 481, 573.

⁹⁴ *T.*, 1918, **113**, 449, 627, 707, 790; compare *Ann. Reports* for 1918 and 1919.

⁹⁵ D. L. Chapman and H. J. George, *Phil. Mag.*, 1921, [vi], **41**, 799; *A.*, ii, 371; compare H. Kallmann, *Z. physikal. Chem.*, 1921, **98**, 433.

⁹⁶ R. T. Lattey, *Phil. Mag.*, 1921, [vi], **41**, 829; *A.*, ii, 426.

aqueous and aqueous solutions has been discussed.⁹⁷ According to the Ostwald-Bredig rule, the value of λ_∞ is related to λ_v , at the dilution v , by the formula $\lambda_\infty = \lambda_v + d_v$, where d_v is a constant depending only on the dilution. If the value of λ_∞ is calculated by the formula $\lambda_\infty = \lambda_v + b'/v^{0.45}$,⁹⁸ the values of d_v can be calculated for each solvent for different dilutions. It was found that the Ostwald-Bredig rule can be applied to water and fifteen organic solvents through the range of dilutions $v = 256$ to $50,000$. From general considerations, it was deduced that the product $d_v \cdot \epsilon \cdot \eta_\infty$ should be constant at a particular dilution for all solvents, ϵ being the dielectric constant and η_∞ the viscosity. This was confirmed, and it was further found that by introducing the dilution factor $v^{0.45}$ an expression is obtained which is general for all solvents (including water) and solutes at all dilutions: $d_v \cdot \epsilon \cdot \eta_\infty \cdot v^{0.45} = \text{const.} = 51.4$. Thus, if ϵ and η_∞ are known for the solvent, d_v can be calculated for any dilution. Thence, from a single observation of λ_v , the value of λ_∞ , and from it $\alpha = \lambda_v/\lambda_\infty$, can be found. It is shown⁹⁹ that the product $\lambda_\infty \eta_\infty$ is constant for all ionising solvents; it is independent of the temperature between 0° and 25° , but depends, within limits, on the nature of the solute. The above general expression may be written $(1 - \alpha)\epsilon \cdot v^{0.45} = 51.4/\lambda_\infty \eta_\infty = \text{const.}$, which shows that, if $\lambda_\infty \eta_\infty$ is known for a salt in any one solvent, its degree of ionisation in any other solvent at any dilution may be calculated. The diameters of ions in aqueous solutions have been calculated¹ from Einstein's diffusion formula: $U = K/N \cdot 6\pi\eta\rho$, where U = velocity, ρ = radius, of particle, K = force acting on particle, N = Avogadro's number, η = viscosity. For most ions, ρ lies between 2.0×10^{-8} cm. and 3.9×10^{-8} cm., but is abnormal for hydrogen (1.1×10^{-8}) and lithium (4.7×10^{-8}). The ionic radii in non-aqueous follow the same order as in aqueous solutions: $\text{H}^+ < \text{K}^+ < \text{Ag}^+ < \text{Na}^+ < \text{Li}^+$; $\text{Br}^- < \text{I}^- < \text{Cl}^- < \text{NO}_3^-$, but in the former the values are about twice as great (mean values 2.67 and 5.33×10^{-8} cm.). Organic anions and kations have the same radius in both solutions (4.4×10^{-8}). Much greater solvation in non-aqueous solutions is assumed.

The sizes of the ions in crystal lattices, calculated by a modification of Born's theory, were found to be,² in 10^{-8} cm.:—Na 0.517; K 0.794; Rb 0.914; F 0.75; Cl 0.953; Br 1.021; I 1.122. The energies of the alkali haloid lattices, in kg. cal., were calculated:

⁹⁷ P. Walden, *Z. anorg. Chem.*, 1920, **113**, 113; *A.*, ii, 170; *ibid.*, 1921, **115**, 49; *A.*, ii, 423.

⁹⁸ R. Lorenz, *A.*, 1920, ii, 6.

⁹⁹ P. Walden, *Z. anorg. Chem.*, 1920, **113**, 85; *A.*, ii, 160.

¹ P. Walden, *ibid.*, 125; *A.*, ii, 171.

² K. Fajans and K. F. Herzfeld, *Z. Physik*, 1920, **2**, 309; *A.*, ii, 174.

NaF 210·4; NaCl 170·0; NaBr 159·7; NaI 146·7; RbBr 146·5; RbI 135·8.

The theory of Hertz has been further developed.³ The value of Hertz's "constant," A , is not 18·9, but is different for each ion. The radii of a number of ions are calculated.

The electrolytic conductivities of a number of molten salts, at temperatures to 1600° have been determined.⁴

The radius of an ion may be calculated⁵ from the formula $W = \frac{1}{2}(1 - 1/\epsilon)N \cdot 2388 \times 10^{-11}e^2z^2/r_i$ Cal., where W = heat of hydration,⁶ N = Avogadro's constant, z = valency, e = charge on electron, r_i = radius of ion, ϵ = dielectric constant of solvent. The values of r_i and of r_a (the atomic radius) are calculated, and it is shown that (except in the case of thallium) for positive ions $r_i < r_a$, whilst for negative ions $r_i > r_a$. This is explained by the increase in volume in the formation of negative ions by the absorption of an electron into the atomic structure, and the decrease in volume when a positive ion is formed by removal of an electron from the atom.

The dissociation of ternary electrolytes has been investigated⁷ in the cases of sulphuric, oxalic, and tartaric acids, and the normal and hydrogen salts of these acids with thallium and potassium. Solutions of concentrations below 0·04*N* follow the law of mass action, and in certain cases this holds at even higher concentrations.

The ionisation of tetramethylammonium thiocyanate (a strong electrolyte) is practically the same ($\alpha = 0\cdot38$) in saturated solutions in nine non-aqueous solvents.⁸ The solubility of the same salt in different non-aqueous solvents is, approximately, given by $\epsilon/\mu^{\frac{1}{2}} = 34$, where ϵ = dielectric constant, μ = molecular solubility.

The "objection" to the electrolytic dissociation theory due to Kahlenberg, and quoted in most text-books, is shown⁹ to rest on inaccurate experiments. Benzene solutions of salts of organic acids (copper oleate, barium erucate, copper stearate, and silver melissate),

³ R. Lorenz, *Z. anorg. Chem.*, 1920, **113**, 131; *A.*, ii, 158; *ibid.*, 135; *A.*, ii, 158; R. Lorenz and P. Osswald, *ibid.*, 114, 209; *A.*, ii, 158; R. Lorenz and W. Neu, *ibid.*, 1921, **116**, 45; *A.*, ii, 481; R. Lorenz and W. Michael, *ibid.*, 161; *A.*, ii, 482; R. Lorenz and A. Scheuermann, *ibid.*, 121, 140; *A.*, ii, 482, 483; compare *Ann. Reports*, 1920.

⁴ F. M. Jaeger and B. Kapma, *ibid.*, 1920, **113**, 27; *A.*, ii, 160.

⁵ M. Born, *Z. Physik*, 1920, **1**, 45; *A.*, ii, 166.

⁶ See *Ann. Reports*, 1920; A. von Weinberg, *Z. Physik*, 1920, **3**, 337; *A.*, ii, 165; A. Reis, *ibid.*, 1920, **1**, 294; *A.*, ii, 166.

⁷ C. Drucker, *Z. physikal. Chem.*, 1920, **96**, 381; *A.*, ii, 161.

⁸ P. Walden, *Z. Elektrochem.*, 1921, **27**, 34; *A.*, ii, 309.

⁹ H. P. Cady and E. J. Baldwin, *J. Amer. Chem. Soc.*, 1921, **43**, 646; *A.*, ii, 309.

which give precipitates with dry hydrogen chloride, showed a conductivity before and during reaction.

Evidence of the ionisation of gases during chemical change has been obtained,¹⁰ in the cases: $\text{Cl}_2 + 2\text{NO} = 2\text{NOCl}$; $2\text{O}_3 = 3\text{O}_2$; and the reaction between ozone and nitric oxide or nitrogen dioxide.

Electromotive Forces.

The use of a saturated KCl-calomel electrode has been proposed¹¹ for use in *E.M.F.* measurements in place of 0.1*N*- and *N*-calomel electrodes. On the assumption that the absolute potential of the *N*-calomel electrode at 25° is 0.5648 volt, that of the saturated potassium chloride electrode is 0.5266 volt, with a temperature coefficient of +0.00020 volt/degree from 5° to 60°. A saturated salt bridge is used.

The hydron concentration in pure water has been found¹² to be 1.23×10^{-8} by a method depending on charging a condenser first with the cell $\text{Hg}|\text{HgCl}_2|\text{KCl}|\text{KCl}|\text{H}_2\text{O}|\text{H}_2$, and then with a standard cell, and in each case discharging through a galvanometer.

Further measurements of the heat of formation of silver iodide by *E.M.F.* methods have been made.¹³ The discrepancy between the results of Fischer¹⁴ and of Jones and Hartmann¹⁵ has been shown to depend on the uncertainty in the correction for I_3' ions in the potassium iodide solution, this being now determined experimentally, and on the use of electrochemically purer silver electrodes by Fischer. The value 15,158 cal. is obtained, which, compared with Fischer's value of 15,169 cal. and that of Jones and Hartmann (14,570), points to the greater accuracy of the former value.

The effect of fluorescent dyes on the *E.M.F.* of illuminated cells has been studied,¹⁶ both alone and in presence of oxidising and reducing substances. The Becquerel effect was observed, and the behaviour of the cells can be explained on the hypothesis of a concealed oxygen-hydrogen photolysis. This has been confirmed¹⁷ by using a fluorescent substance in an electrolytic cell, when a depolarising action was clearly noticed.

The thermodynamic treatment of concentrated solutions, with

¹⁰ A. Pinkus and M. de Schulthess, *J. Chim. phys.*, 1920, **18**, 366; *Helv. Chim. Acta*, 1921, **4**, 288; *A.*, ii, 368; compare O. W. Richardson, *Phil. Trans.*, 1921, [A], **222**, 1; *A.*, ii, 422.

¹¹ H. A. Fales and W. A. Mudge, *J. Amer. Chem. Soc.*, 1920, **42**, 2434; *A.*, ii, 79.

¹² H. T. Beans and E. T. Oakes, *ibid.*, 2116; *A.*, ii, 12.

¹³ O. Gerth, *Z. Elektrochem.*, 1921, **27**, 287; *A.*, ii, 534.

¹⁴ *A.*, 1912, ii, 536, 1054.

¹⁵ *Ibid.*, 1915, ii, 308.

¹⁶ E. Staechelin, *Z. physikal. Chem.*, 1920, **94**, 542; *A.*, 1920, ii, 580.

¹⁷ E. Baur, *Z. Elektrochem.*, 1921, **27**, 72; *A.*, ii, 236.

special reference to the *E.M.F.*'s of amalgams, has been developed.¹⁸ The electromotive properties of a number of binary alloys have been studied.¹⁹ With thallium and thallium-lead alloys, the potentials with 0 to 20 atom. per cent. of lead are practically equal to those of thallium; from 50 to 100 atom. per cent. of lead they are equal to the lead potentials; between 20 and 50 atom. per cent. of lead the potentials pass into one another asymptotically.

Experiments on thermo-elements²⁰ showed that copper-phosphorus alloys did not give a favourable ratio of thermal to electrical conductivity, which is inversely proportional to the efficiency of a thermo-couple. Antimony-cadmium alloys with approximately atomic composition show probably the highest thermoelectric power of all metals and alloys hitherto investigated. The influence of heat treatment is of importance in investigating the effect of temperature on *E.M.F.* Amalgamation depresses thermoelectric power. The effect of pressure on a solid junction of two materials has been calculated²¹ on the assumption of material transport with the current. The measurement of the resulting "bary-electromotive force" would give the transport numbers in solid electrolytes and the ratio of electronic to material conduction in poor conductors.

Chemical Dynamics and Equilibrium.

An investigation²² of the catalytic decomposition of hydrogen peroxide by sodium iodide in aqueous mixtures of alcohols, glycerol, and pyridine failed to disclose any relation between the velocity of reaction and the dielectric constant, viscosity, or surface tension of the pure solvent; the latter appears to exert a specific influence. The effect of mercuric ions on the velocity of oxidation of arsenious acid by nitric acid is peculiar.²³ At a concentration of 7.7×10^{-6} mol. per litre the reaction was completely inhibited. With diminishing concentration, the inhibiting effect of the mercuric ions became less marked down to a concentration of 7.7×10^{-8} ,

¹⁸ G. N. Lewis and M. Randall, *J. Amer. Chem. Soc.*, 1921, **43**, 233; *A.*, ii, 241.

¹⁹ R. Kremann, *Z. Metallkunde*, 1920, **12**, 185; *Chem. Zentr.*, 1920, iii, 684; *A.*, ii, 10; R. Kremann and H. Ruderer, *ibid.*, 1920, **12**, 209; *Chem. Zentr.*, 1920, iii, 684; *A.*, ii, 11; R. Kremann and J. Gmachl-Pammer, *Int. Z. Metal.*, 1920, **12**, 241; *Chem. Zentr.*, 1921, i, 123; *A.*, ii, 156.

²⁰ G. Pfeleiderer, *Ges. Abhandl. Kennt. Kohle*, 1919, **4**, 409; *Chem. Zentr.*, 1921, i, 348; *A.*, ii, 296; F. Fischer and G. Pfeleiderer, *ibid.*, 440; *Chem. Zentr.*, 1921, i, 349; *A.*, ii, 296.

²¹ M. Polányi, *Z. physikal. Chem.*, 1921, **97**, 459; *A.*, ii, 372.

²² Van L. Bohson, *J. Physical Chem.*, 1920, **24**, 677; *A.*, ii, 185.

²³ A. Klemenc and F. Pollak, *Z. anorg. Chem.*, 1921, **115**, 131; *A.*, ii, 442.

and at 7.7×10^{-9} there was a positive catalytic effect, which became still more marked at 7.7×10^{-11} mol. per litre. The smallest measured effective concentration of catalyst previously recorded is 7×10^{-6} for colloidal platinum in the decomposition of hydrogen peroxide.

The kinetics of the reduction of azo-compounds by acid stannous chloride has been studied.²⁴ The reaction is bimolecular, and in cases where the azo-compound is broken up into two amino-derivatives it occurs in two stages. The reduction to hydrazo-compound takes place first with measurable velocity; further reduction then occurs with extreme rapidity.

The kinetics of the formation of acetone from acetoacetic acid in acid and in alkaline solution has been studied.²⁵ In the second case, practically only the anion $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2'$, whilst in strongly acid solution practically only undissociated acetoacetic acid, is present. The undissociated and dissociated acids show very different velocities of decomposition; that of the former is fifty times the greater. In almost neutral solutions, the rate of decomposition depends on the ionisation of the acid.

Many reactions having large temperature coefficients are sensitive to light,²⁶ hence it is concluded that sensitiveness to temperature and to light influences have a common cause, in agreement with Perrin's radiation hypothesis.²⁷

A number of abnormally large and small temperature coefficients have been explained²⁸ by hydrolysis of some salt present. The reaction between iodic acid and potassium iodide in dilute solutions is very rapid at 0° . In presence of sodium and magnesium sulphates, slightly less iodine is liberated at higher than at lower temperatures. This apparent negative coefficient is due to hydrolysis of the sulphate at higher temperatures, with formation of OH' ions. The abnormally large temperature coefficient of the reaction $3\text{I}_2 + 6\text{OH}' = 5\text{I}' + \text{IO}_3' + 3\text{H}_2\text{O}$ in presence of sodium carbonate and sodium hydrogen carbonate is due to hydrolysis of these salts.

A study²⁹ of induced reactions led to the hypothesis that the substance in which oxidation is induced (sodium arsenite) acts as a negative catalyst towards the substance which induces the

²⁴ H. Goldschmidt and A. Braanaas, *Z. physikal. Chem.*, 1920, **96**, 180; *A.*, ii, 184.

²⁵ E. M. P. Widmark, *Acta Med. Scandinav.*, 1920, **53**, 393; *Chem. Zentr.*, 1921, i, 9; *A.*, ii, 183.

²⁶ N. R. Dhar, *Proc. K. Akad. Wetensch. Amsterdam*, 1920, **23**, 308; *A.*, ii, 37.

²⁷ *A.*, 1919, ii, 177.

²⁸ N. R. Dhar, *Proc. K. Akad. Wetensch. Amsterdam*, 1920, **23**, 313; *A.*, ii, 37.

²⁹ *Idem, ibid.*, 1921, **23**, 1074; *A.*, ii, 391.

oxidation (sodium sulphite). The formation of a complex of the two oxidisable substances, the less oxidisable constituent of which is more easily oxidised, is assumed.

In a study of the keto-enolic tautomerism of benzoylcamphor,³⁰ it was found that the results obtained by K. H. Meyer's method³¹ of titration with bromine do not agree with the equation $c_A/c_B = Kl_A/l_B$, where c_A , c_B are the equilibrium concentrations, l_A , l_B the solubilities, and K is a constant independent of the nature of the solvent.³² When the method of optical activity³³ was used, a satisfactory agreement was found, and the ratios of the enol/ketone forms in equilibrium in different solvents were found to be: in toluene, 82/18; in alcohol, 61/39; in acetone, 52/48. At -83° , both forms should co-exist in the crystalline state.

A new method for the determination of the vapour pressure of salt hydrates is described.³⁴ It consists in the establishment of equilibrium between the hydrates and a solution of water in iso-amyl alcohol, followed by an estimation of the water content of the resulting liquid. (With salts of small vapour pressure, a simple method would appear to be a determination of the freezing point of benzene in equilibrium with the salt.)

Variations with time in the activity of colloidal platinum have been studied.³⁵ The catalytic power is attributed to a metal-oxygen complex, and the initial rise of activity to increase of oxygen concentration. The oxide theory is also supported by other workers.³⁶

The conditions which control the accuracy of titration of mixtures of acids and bases, from the point of view of suitable choice of indicator, have been described.³⁷

The increase in size of particles of a precipitate in contact with a liquid is usually ascribed to the (experimentally verified) difference in solubility of large and small crystals. It has been suggested³⁸ that it is due to "irreversible transformation of secondary aggre-

³⁰ H. Vixeboxse, *Rec. trav. chim.*, 1921, **40**, 1; *A.*, ii, 179.

³¹ *A.*, 1911, i, 350, 832.

³² Van't Hoff, quoted by Dimroth, *A.*, 1911, ii, 31; 1913, ii, 763; compare Smits, *A.*, 1915, ii, 750.

³³ M. O. Forster, *T.*, 1901, **79**, 987.

³⁴ R. E. Wilson, *J. Amer. Chem. Soc.*, 1921, **43**, 704; *A.*, ii, 376; A. A. Noyes and L. R. Westbrook, *ibid.*, 726; *A.*, ii, 377.

³⁵ A. de G. Rocasolano, *Compt. rend.*, 1921, **173**, 41, 234; *Anal. Fis. Quím.*, 1920, **18**, 308, 361; 1921, **19**, 114; *A.*, 1920, ii, 479, 607; 1921, ii, 251, 321, 390, 498, 542.

³⁶ R. Willstätter and E. Waldschmidt-Leitz, *Ber.*, 1921, **54**, [B], 113; *A.*, ii, 185.

³⁷ H. T. Tizard and A. R. Boeree, *T.*, 1921, **119**, 132.

³⁸ S. Odén, *Svensk. Kem. Tidskr.*, 1920, **32**, 108; *A.*, ii, 25.

gates primarily formed." Reversibility appears to depend on the degree of hydration of the particles which are attached to one another by aqueous envelopes. If these are broken, or if the original hydration is too slight (for example, with metallic particles) the transformation becomes irreversible.

The effect of one solute, A , in lowering the solubility of a second solute, B , in a given solvent has been shown to be represented³⁹ by the simple equation $\log (s_0/s) = kc$, where s_0 , s are the solubilities of B in the pure solvent and in a solution of A in B of concentration c , and k is a constant.

Heterogeneous Reactions.

The influence of physical conditions on the velocity of decomposition of some crystalline solids was investigated⁴⁰ in the cases of the evolution of gas by heat from silver permanganate, potassium permanganate, ammonium dichromate, and solid solutions of potassium permanganate and potassium chlorate. The conclusion is drawn that the rate of decomposition is largely dependent on the surface of the solid, that the effective surface is considerably greater than the apparent surface, and that solid crystals may be assumed to be aggregates loosely held together. The results with solid solutions support the hypothesis that the process of solid mixture leads to increased chemical stability, from the heat of mixture.

The reduction of cotton-seed oil by hydrogen in presence of metallic nickel at 180° ⁴¹ shows that the variations in catalytic power of reduced nickel may be referred to the different surfaces of nickel exposed. In the catalytic reduction of ethylene to ethane in presence of nickel, an induction period was noticed,⁴² followed by a sharp maximum velocity. It is supposed that hydrogen is selectively adsorbed, whilst ethylene is adsorbed only after activation (chiefly by "thermal contact" with a molecule undergoing hydrogenation). The nickel at first becomes covered with hydrogen molecules. Reaction of these with ethylene molecules occurs, the heat liberated being communicated to the surrounding molecules. Hydrogen is then volatilised and activated ethylene deposited.

The relation between the occlusive power of palladium for hydrogen and its catalytic activity has been studied,⁴³ lead being

³⁹ P. C. L. Thorne, *T.*, 1921, **119**, 262; compare W. Nernst, *Z. physikal. Chem.*, 1890, **6**, 16.

⁴⁰ C. N. Hinshelwood and E. J. Bowen, *Proc. Roy. Soc.*, 1921, [A], **99**, 203; *A.*, ii, 443; compare *Phil. Mag.*, 1920, [vi], **40**, 569; *A.*, 1920, ii, 743.

⁴¹ E. F. Armstrong and T. P. Hilditch, *ibid.*, 490; *A.*, 1920, ii, 582.

⁴² D. M. and W. G. Palmer, *ibid.*, 402; *A.*, ii, 541.

⁴³ E. B. Maxted, *T.*, 1921, **119**, 1280.

the inhibitant. The relation is linear from the point corresponding with zero concentration of the poison up to a stage where the greater part of the activity has been suppressed. In this region a point of inflexion occurs, beyond which the rate of decrease in catalytic activity due to further addition of lead falls off much less rapidly than on the main part of the curve. The amount of lead required to reduce the catalytic activity to half is very much less than that which reduces the occlusive power to half its original value. This may be explained by the fact that, whilst the occlusion is not confined to the surface, catalysis is mainly a surface phenomenon. Measurements of the adsorption of gases by metallic catalysts⁴⁴ show that it is a specific property of the metal, depending on the mode of preparation, being less the higher the temperature to which the metal has been subjected. Destruction of catalytic activity is accompanied by almost complete suppression of adsorptive power. Maximum catalytic activity does not occur at temperatures at which maximum adsorption is shown. A strong or irreversible adsorption of any one of the reacting substances tends to render the catalyst inactive. Reaction is the resultant of two factors, adsorption and temperature. The adsorptive capacity is an index of the temperature at which reaction can be induced. Where adsorption is strong, a lower temperature may effect interaction.

Combustion and Explosion Reactions.

The mechanism of reaction in some cases of combustion has been studied⁴⁵ and the conclusion is drawn that reaction is preceded by the formation of an unstable additive compound. The minimum amount of moisture necessary to promote explosion of carbon monoxide with oxygen or nitrous oxide corresponds with a partial pressure of 0.5 mm. The reaction is formulated as follows: (1) $\text{CO} + \text{H}_2\text{O} = \text{H}\cdot\text{CO}_2\text{H}$; (2) $\text{H}\cdot\text{CO}_2\text{H} = \text{CO}_2 + \text{H}_2$; (3) $\text{H}_2 + \text{O}_2 = \text{H}_2\text{O}_2$; (4) $\text{H}_2\text{O}_2 = \text{H}_2\text{O} + \text{O}$. The presence of hydrogen in the carbon monoxide flame was proved by its passage through palladium. Hydrogen peroxide was detected when the gas was passed through a heated quartz tube, cooled in the further part. An indication of a peroxide-like substance was also obtained in the combustion of cyanogen.

The influence of carbon dioxide on the pressure limit of phosphorescence of phosphorus in oxygen and on the inferior limits of explosion of hydrogen and methane is greater than that of

⁴⁴ H. S. Taylor and R. M. Burns, *J. Amer. Chem. Soc.*, 1921, **43**, 1273; *A.*, ii, 630.

⁴⁵ H. von Wartenberg and B. Sieg, *Ber.*, 1920, **53**, [B], 2192; *A.*, ii, 107.

nitrogen.⁴⁶ The point of inflammation of various mixtures of hydrogen and oxygen, defined as the temperature at which the reaction velocity exceeds a measurable value, has been measured⁴⁷ by bringing both gases to the required temperature and determining by a membrane manometer whether rapid reaction occurs on mixing. The minimum inflammation point, 397.5° , was found with $3\text{H}_2 + 2\text{O}_2$; for $\text{H}_2 + \text{O}_2$ it is 407° , and increases after the minimum to 433° for $4\text{H}_2 + \text{O}_2$ (in all cases for dry gases). With moist gases, the results were rather irregular. The reaction between moist oxygen and hydrogen is bimolecular; with absolutely dry gases, it would seem to be termolecular. The possibility of velocity measurements is discussed.

A detailed study of the propagation of combustion in gaseous mixtures from the point of view of Hugoniot's law has appeared.⁴⁸ The phenomenon of successive explosions has also been investigated.⁴⁹ Measurements of the heat loss by conduction and radiation during the explosion and subsequent cooling of mixtures of coal gas and air indicate⁵⁰ that at the moment of maximum pressure about 10 per cent. of the heat of combustion has not been converted into thermal energy and that after-burning continues for at least 0.25 sec. after the attainment of the maximum pressure.

Reference may be made to the important monograph on the properties of explosives contributed in a special lecture to the Society.⁵¹

A piezoelectric method of measuring explosion pressures has been described.⁵²

The modes of ignition of mixtures of hydrogen and of carbon monoxide with oxygen have been studied⁵³ by measurements of the rate of rise of pressure. In the second case, there is a slower rise of pressure and evolution of heat for a relatively long time after the attainment of the maximum pressure.

Colloids.

Determinations of the radii of ultramicroscopic gold and silver particles (*a*) from the colour, (*b*) from the Brownian movement,

⁴⁶ W. P. Jorissen, *Rec. trav. chim.*, 1920, **39**, 715; *A.*, ii, 99; compare *A.*, 1919, ii, 62.

⁴⁷ H. Fiesel, *Z. physikal. Chem.*, 1921, **97**, 158; *A.*, ii, 317.

⁴⁸ L. Crussard, *Technique moderne*, 1920, **12**, 243, 295; *A.*, ii, 32.

⁴⁹ A. Stavenhagen and F. Schuchard, *Z. angew. Chem.*, 1920, **33**, 286; *A.*, ii, 33.

⁵⁰ W. T. David, *Proc. Roy. Soc.*, 1921, **98**, [A], 303; *A.*, ii, 85.

⁵¹ (Sir) R. Robertson, *T.*, 1921, **119**, 1.

⁵² D. A. Keys, *Phil. Mag.*, 1921, [vi], **42**, 473; *A.*, ii, 628.

⁵³ W. A. Bone and W. A. Haward, *Proc. Roy. Soc.*, 1921, [A], **100**, 67; *A.*, ii, 628.

showed no systematic variation between the two series.⁵⁴ The degree of dispersity of sols with particles so small as to be invisible in the ultramicroscope may, as is known,⁵⁵ be found by allowing the particles to act as nuclei for the deposition of gold. This method of "gilding" has been⁵⁶ applied to determine the radius of amicros. Smoluchowski's formula⁵⁷ for the velocity of flocculation is verified⁵⁸ for the rapid, but not for the slow, flocculation of a selenium sol. The limiting size of a particle which exhibits Brownian movement has been found⁵⁹ to be 2.6μ for a number of metals. In different liquids, the logarithm of the limiting size was found to give a straight line when plotted against the viscosity: $a\eta^{0.229} = 3.5$ for gold; $a\eta^{0.249} = 3.4$ for copper.

A series of investigations on soap curds⁶⁰ has confirmed and extended the ultramicroscopic investigations of Zsigmondy and Bachmann.⁶¹ It is shown that soap may exist in three distinct hydrated forms: sol and gel (transparent) and curd (opaque).

The physical-chemical analysis of ferric hydroxide sols shows⁶² that this substance is a complex salt of the type $x\text{Fe}(\text{OH})_3y\text{Fe}/\text{An}$, where An is the anion in presence of which the sol is formed.

The modulus of rigidity of gelatin gels at different concentrations, under torsion, follows Hooke's law nearly up to the breaking point.⁶³ The modulus of elasticity, E , and the concentration, c , are related by $E = kc^n$ over a limited range, but the constants k and n differ for different grades of gelatin. The elasticity is not a simple function of the hydrogen-ion concentration. Gelatin gels may represent any transition stage between a two-phase structure and a physically homogeneous system in which mechanical strength must be attributed to solution forces.

Three-phase emulsions may be obtained⁶⁴ by shaking pairs of immiscible liquids, such as water and benzene, with alumina, zinc

⁵⁴ R. Fürth, *Physikal. Z.*, 1921, **33**, 80; *A.*, ii, 243.

⁵⁵ Zsigmondy, *A.*, 1906, ii, 679.

⁵⁶ G. Börjeson, *Kolloid Z.*, 1920, **27**, 18; *A.*, ii, 27.

⁵⁷ *A.*, 1917, ii, 297.

⁵⁸ H. R. Kruyt and A. E. van Arkel, *Rec. trav. chim.*, 1920, **39**, 656; *A.*, ii, 25 (compare *A.*, 1919, ii, 140; 1920, ii, 739); *ibid.*, 169; *A.*, ii, 312.

⁵⁹ B. Arakatsu and M. Fukuda, *Mem. Coll. Sci. Kyoto*, 1920, **4**, 179; *A.*, ii, 175.

⁶⁰ J. W. McBain, W. F. Darke, and C. S. Salmon, *Proc. Roy. Soc.*, 1921, [*A*], **98**, 395; *A.*, ii, 312; McBain and M. E. Laing, *T.*, 1920, **117**, 1506; McBain and H. E. Martin, *ibid.*, 1921, **117**, 1369; McBain and Salmon, *ibid.*, 1374.

⁶¹ *A.*, 1913, ii, 194.

⁶² W. Pauli, *Kolloid Z.*, 1921, **28**, 49; *A.*, ii, 246.

⁶³ S. E. Sheppard and S. S. Sweet, *J. Amer. Chem. Soc.*, 1921, **43**, 539; *A.*, ii, 311.

⁶⁴ H. Bechold, L. Dede, and L. Reiner, *Kolloid Z.*, 1921, **28**, 6; *A.*, ii, 177.

dust, or yeast, and an "emulsion promoter," such as pyridine, acetic acid, ethyl alcohol, or sodium nitrate. The relative surface tensions of the two liquids have no influence on the emulsification.

The influence of the concentration of a sol on the coagulative power of any given ion has been investigated.⁶⁵ For univalent ions, the concentration to produce coagulation increases with decreasing concentration of the colloid, very rapidly at low values of the latter. For bivalent ions, the ion concentration is almost constant, and thus independent of the concentration of the colloid. For trivalent ions, the coagulating concentration is almost proportional to the colloid concentration. At least two properties of the system colloid + electrolyte seem to be involved. The influence of dilution and quantity of electrolyte on flocculation has also been considered.⁶⁶ The velocity of flocculation, with a constant quantity of electrolyte and colloid, at first diminishes as the dilution of electrolyte increases, but tends to a limit when the dilution reaches a certain value. When the amount of electrolyte is varied but the concentration kept constant, the velocity of flocculation increases with the amount of electrolyte used.

In a study⁶⁷ of the swelling of gelatin, it is concluded that the swelling is the result of osmotic pressure within the gel, the latter acting as an imperfectly resisting membrane.

Investigations on proteins⁶⁸ show that the Hofmeister series is not the correct expression of the relative effects of ions on the swelling of gelatin. The valency, not the nature, of the ion in combination with gelatin affects the degree of swelling. Results depend on the effect of the salt added on the hydrogen-ion concentration of the protein solution.

The electro-endosmose of a number of solutions with various membranes has been investigated.⁶⁹ The charge on which the electro-endosmosis depends can be attributed to ionic adsorption.

The precipitation of colloids by electrolytes has been considered⁷⁰ from the point of view of the surface forces exerted by heteropolar crystal lattices on adsorbed ions. The results were confirmed by measurements of the adsorption of thorium-*B* by silver haloids. Those ions are strongly adsorbed by an ionic space lattice which

⁶⁵ E. F. Burton and E. Bishop, *J. Physical Chem.*, 1920, **24**, 701; *A.*, ii, 176.

⁶⁶ A. Boutaric and M. Vuillaume, *Compt. rend.*, 1921, **173**, 229; *A.*, ii, 537.

⁶⁷ C. R. Smith, *J. Amer. Chem. Soc.*, 1921, **43**, 1350; *A.*, i, 749.

⁶⁸ J. Loeb, *J. Gen. Physiol.*, 1920, **3**, 247; *A.*, i, 136; *ibid.*, 1921, **3**, 391; *A.*, i, 367; compare *A.*, 1920, i, 894.

⁶⁹ A. Gyemant, *Kolloid Z.*, 1921, **28**, 103; *A.*, ii, 298.

⁷⁰ K. Fajans and K. von Beckerath, *Z. physikal. Chem.*, 1921, **97**, 478; *A.*, ii, 386.

forms sparingly soluble compounds with the oppositely charged constituent of the lattice.

It has been shown that arsenic trisulphide sols are photochemically active.⁷¹ Colloidal sulphur is formed by exposure to light.

The precipitation of arsenious sulphide sols by cobaltammine ions has been applied⁷² to determine the valency of the ions. The limiting concentration of the precipitating solution can be expressed by the formula $S_N = S_1/N^4$, where S_N is the equivalent concentration of an N -valent ion and S_1 the limiting concentration for a univalent ion. This is deduced theoretically from the adsorption formula.

A comparison of the protective effect, and the inhibiting influence on catalytic decomposition, of colloids,⁷³ has shown that the two are parallel. Soaps are regarded as colloidal even at great dilution.

Adsorption.

Freundlich's rule, that the order in which substances are adsorbed is almost independent of the nature of the solid phase, has been confirmed⁷⁴ with various kinds of charcoal. Except in the case of iodine, the adsorption isotherm, $x/m = \alpha c^{1/n}$ was found to hold, the constant α being taken as an index of the adsorptive power. The adsorption of iodine by carbon in different forms, in benzene and chloroform, has been studied⁷⁵ over periods of time extending to five years. A rapid condensation of iodine takes place in the first few minutes, followed by a much slower "sorption" continuing for months or years. The first condensation is attributed to true adsorption, the second to slow absorption.

The adsorption of salts by silver powder⁷⁶ lends support to Polányi's theory⁷⁷ that the adsorbed ions form several molecular layers.

The adsorption equilibrium between fatty acids in aqueous solution and charcoal is displaced⁷⁸ by neutral salts in the sense that more acid is adsorbed. The amounts of cation and anion adsorbed by carefully purified charcoal from aqueous solutions of

⁷¹ H. Freundlich and A. Nathansohn, *Kolloid Z.*, 1920, **28**, 258; *A.*, ii, 494.

⁷² K. Matsuno, *J. Coll. Sci. Tokyo*, 1921, **41**, ii, 1; *A.*, ii, 637.

⁷³ T. Iredale, *T.*, 1921, **119**, 109, 625.

⁷⁴ I. M. Kolthoff, *Pharm. Weekblad*, 1921, **58**, 630; *A.*, ii, 383.

⁷⁵ J. B. Firth, *Trans. Faraday Soc.*, 1921, **16**, 434; *A.*, ii, 382.

⁷⁶ H. von Euler and A. H. Hedelius, *Arkiv Kem. Min. Geol.*, 1920, **7**, No. 31, 1; *A.*, ii, 490.

⁷⁷ M. Polányi, *Ber. Deutsch. Physik. Ges.*, 1916, **18**, 76; *A.*, 1916, ii, 474.

⁷⁸ G. Wiegner, J. Magasanik, and A. J. Virtanen, *Kolloid Z.*, 1921, **28**, 51; *A.*, ii, 244.

alkali nitrates are equivalent in all cases.⁷⁹ The adsorption increases with the atomic weight of the kation, and the same holds with nitrates of alkaline earths. Experiments with potassium and barium salts showed that the adsorption of halogen anions increases with the atomic weight. The variation with the kation is not considerable. With other salts, the order of adsorption varies with concentration. The negative adsorption of alkali haloids by wood charcoal has been measured.⁸⁰

The simultaneous adsorption of solvent and solute has been examined⁸¹ in the system benzene-iodine-charcoal. Equilibrium was attained through the vapour phase, and the temperature of the charcoal was kept above that of the liquid. The adsorption of benzene from iodine solutions was less than that from pure solvent. A comparison of the adsorption of water and alcohol by charcoal⁸² showed that the alcohol is adsorbed to nearly five times the extent of water. The result is not in agreement with Langmuir's opinion⁸³ that equal volumes should be adsorbed.

Osmosis.

An equation for the osmotic pressure of mixtures has been deduced.⁸⁴ The freezing-point depressions of pairs of non-electrolytes in concentrated solutions were determined separately and in admixture. The osmotic pressure of the mixture may be less or greater than the sum of the partial osmotic pressures. The facts are explained by van der Waals's theory of binary mixtures.

Donnan's theory of membrane equilibrium⁸⁵ has been applied⁸⁶ to the colloidal behaviour of proteins. Gelatin chloride solutions (P_H 3.5) containing various concentrations of sodium nitrate, in collodion bags, were placed in aqueous hydrochloric acid (P_H 3.0) containing similar concentrations of sodium nitrate. With increasing concentrations of neutral salt, the potential difference between the two solutions was depressed in the same proportion as the osmotic pressure of the gelatin chloride solution. The potential

⁷⁹ S. Odén and H. Andersson, *J. Physical Chem.*, 1921, **25**, 311, *A.*, ii, 438; S. Odén and E. W. Langelius, *ibid.*, 385; *A.*, ii, 625.

⁸⁰ A. Pickles, *T.*, 1921, **119**, 1278.

⁸¹ A. M. Bakr and J. E. King, *ibid.*, 454.

⁸² J. Driver and J. B. Firth, *ibid.*, 1126.

⁸³ *J. Amer. Chem. Soc.*, 1917, **39**, 1848.

⁸⁴ R. Cernatesco, *Ann. Sci. Univ. Jassy*, 1920, **10**, 259; *Chem. Zentr.*, 1921, iii, 199; *A.*, ii, 576.

⁸⁵ *Z. Elektrochem.*, 1911, **17**, 572; *A.*, 1911, ii, 848; *T.*, 1911, **99**, 1554; 1919, **115**, 1313.

⁸⁶ J. Loeb, *J. Gen. Physiol.*, 1921, **3**, 557, 667, 691; *A.*, i, 368, 627; compare *A.*, 1920, ii, 14, 234, 358, 476, 477, 602.

differences agreed with those calculated by Nernst's formula on the assumption that they were due to P_H . The effect of salts on the swelling or viscosity of gelatin chloride is similar. The results are explained by an unequal distribution of non-colloid ions on the two sides of the membrane. Proctor's expression ⁸⁷ for the Donnan equilibrium is verified. Electro-osmose in liquids of low conductivity has been studied ⁸⁸ by driving a liquid through a capillary tube and measuring the *E.M.F.* A proportionality was found to exist between the *E.M.F.* and the external pressure, as required by theory. A marked increase in the conductivity of a badly conducting liquid raises the potential difference at the surface of contact with the solid.

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⁸⁷ *T.*, 1914, **105**, 313; 1916, **109**, 307.

⁸⁸ W. Ślászewski, *Krakau Anzeiger*, 1917, [A], 269; *Chem. Zentr.*, 1920; iii, 782; *A.*, ii, 13.