

(W.-M.) has a value almost exactly five times smaller than the theoretical "Bohr-magneton." Weiss obtained his values for the atomic magnetic moments of ions in solutions from the measured susceptibilities χ by means of Langevin's formula based on classical statistics

$$(3) \quad 4\pi\chi = \frac{Nm^2}{3kT}$$

Where N denotes the number of atoms (or ions) in unit space, k Boltzmann's constant and T the temperature. Cabrera uses the same method of theoretical analysis and derives values of m in Weiss-magnetons as units.

It has been, however, pointed out by W. Pauli (*Phys. Zeitschr.* 1920, xxi, p. 615) that the statistics of the quantum theory lead to a different result and that Langevin's formula must be replaced by the new one

$$(4) \quad 4\pi\chi = \frac{(j+1)(2j+1)}{6j^2} \frac{Nm'^2}{kT}$$

We see that from the point of view of the quantum theory the values m derived by Cabrera need a correction, and that the new value m' will be $m' = \alpha m$, where the correction factor α has the form

$$(5) \quad \alpha = \frac{j}{\sqrt{(j+1)(j+\frac{1}{2})}}$$

$j:$	1	2	3	4	5	6
$\alpha:$	0.577	0.730	0.802	0.842	0.870	0.890

The application of these considerations to Cabrera's material is contained in a following table. The second column gives the values of m in Weiss-magnetons, which this author considers as the best mean of the results of different observers. It may be remarked that some of the authors find values lying rather far from whole numbers, so that the integral nature of this quantity does not seem quite assured to the unprejudiced observer. In order to find the corrected value m' , it is necessary to make a hypothesis as to the number j of Bohr-Magnetons in the atom. This hypothetical j is given in the third column, while the fourth contains the result of the correction in Weiss-Magnetons, from which the value of m' in Bohr-Magnetons is obtained by dividing by five (fifth column). The agreement of the final result of the fifth column with the hypothetical j of the third gives a measure of the extent to which the hypothesis was justified. It will be remembered that j represents the number of

Bohr-Magnetons m_0 contained in an atom, so that the third column gives our hypothesis as to this number, while the fifth contains the same number as derived from Cabrera's experimental material. We see that there exists an apparent discrepancy in Ni^{++} in saturated salts and for Fe^{++} . However, the case of Fe^{++} is without any significance, because the uncertainty of the experimental values is here so large as to prevent any conclusions. The rest of the paramagnetic salts shows an excellent agreement with the quantum theory.

There may be suggested still another and more convenient method for checking these results. By means of formula (3) we can compute the susceptibilities (referred to the gram-atom of material) corresponding to the individual integer j . We have tabulated these values of the susceptibility in the sixth column, while in the seventh the actually measured values are given for comparison.

Again we see that a discrepancy larger than the limits of experimental error exists only for Ni . Physicists engaged in magnetic research would therefore promote the development of the theory of quanta by paying particular attention to the ions Fe^{++} and Ni^{++} .

PAUL S. EPSTEIN

NORMAN BRIDGE LABORATORY OF PHYSICS,
CALIFORNIA INSTITUTE OF TECHNOLOGY

THE AMERICAL CHEMICAL SOCIETY

DIVISION OF PHYSICAL AND INORGANIC CHEMISTRY

Robert E. Wilson, *chairman*

Graham Edgar, *secretary*

Section I. General Inorganic and Physical Chemistry.

Studies by a new method of analysis of complex crystal structures and normally and abnormally reflected secondary X-rays characteristic of chemical elements in crystals: GEORGE L. CLARK. (1) A new ionization spectrometer method of analyzing crystals has been designed to be applicable to variable parameter systems (triclinic, monoclinic, orthorhombic), and to be independent of previous determinations of structure, number of molecules per unit, wave-length and densities. Wave-lengths producing particular effects are accurately evaluated by an experimental determination of the critical voltage in the quantum law $Ve = hc/\lambda$. (2) By this method crystals and powders of the following compounds have been

studied and structures determined; KI, simple cubic, $d = 3.532$; CsI, cube-centered, $d = 4.562$; KI_3 , cube-centered slightly distorted into monoclinic prism, $d_{100}^b = 4.70$; CsI_3 , orthorhombic, $d_{100} = 4.50$, $d_{010} = 6.43$, $d_{001} = 7.02$, 3 I atoms on body diagonal; $CsIBr_2$, orthorhombic, $d_{100} = 4.26$, $d_{010} = 5.91$, $d_{001} = 6.90$, CsI and Br planes equally spaced for 100 series. (3) New phenomena of great importance have been incidentally discovered: (1) the production of secondary X-rays characteristic of elements I, Cs and Br in crystals, appearing alone in spectra when the potential is below that required for the generation of the line spectrum of the target element tungsten, obeying the law $n\lambda = 2d \sin \theta$, and enabling distinction between Cs and I in the same crystal; (2) in addition the abnormal reflection of characteristic Iodine rays from KI, varying in direction in an anomalous fashion with the angle of incidence, corresponding to no one set of planes, not obeying the usual laws and unexplainable by present theories. These things have direct bearing upon the mechanism of X-ray reflection and excitation, orientation, damping, electronic structure, mutual atomic effects.

Electron positions in crystals: MAURICE L. HUGGINS. A careful analysis of the various conceivable ways in which the valence electrons or electron orbits might be distributed in crystals such as C, Si, Ge, SiC, ZnS, AgI, AgCl, NaCl, etc., based solely on the assumptions: (1) that the arrangements of atomic centers in the crystals have been correctly determined by means of X-rays, (2) that these arrangements are due to the attractions and repulsions between nuclei and electrons, and (3) that the number of valence electrons is 1 for Na and Ag, 2 for Zn, 4 for C, Si and Ge, 6 for S, 7 for Cl, Br and I, etc., shows that the valence electrons in these compounds must be in relatively fixed positions in pairs at tetrahedron corners around the kernel of each electronegative atom. In some cases they also form a tetrahedron of pairs around the kernel of each electropositive atom. This conclusion is in accord with the observation that, assuming only (1) and (3) above, the number of valence electrons in every crystal containing electronegative atoms whose structure has been determined by X-rays, excepting only Cr, Mo, Ta, W and the trihalides, is precisely the number required for a tetrahedron of pairs around the kernel of each electronegative atom. Furthermore, this result is predictable, without any new assumptions being necessary, from the system of atomic structures previously proposed (*J. Phys. Chem.*, xxvi, 601, 1922).

The determination of crystal structures without

X-rays: MAURICE L. HUGGINS. A study of the arrangements of valence electrons in crystals whose atomic arrangements have been determined by means of X-rays has made it possible to predict the structures of many crystals and in some cases to verify these predictions by means of data other than that obtained by X-rays. The crystals considered, besides a number whose structures have been determined by X-rays, include ZnTe, CdSe, CdTe, HgS, HgSe, HgTe, AuCl, BN, BP, AlN, AlP, AlAs, SiO_2 (cristobalite), TiO_2 (rutile and anatase), SnO_2 (cassiterite), MnO_2 (polianite), Mn_2O_3 , Mn_3O_4 and Al_4C_3 . In each case the assumption that the electrons are in pairs at tetrahedron corners around each atomic kernel (compare preceding abstract), and the available crystallographic data are sufficient to limit the number of possible structures to 1 or 2. These structures are checked up chiefly by comparisons of interatomic distances.

Further interesting tracks of alpha particles in gases (lantern): R. W. RYAN AND W. D. HARKINS.

A new relation concerning the periodic system of the isotopes (lantern): W. D. HARKINS.

On the disintegration of atoms: W. D. HARKINS.

The separation of mercury into isotopes in a steel apparatus (lantern): W. D. HARKINS AND S. L. MADORSKY.

The relation between thermoelectric force and the rate of evaporation of electrons from hot filaments: WORTH H. RODEBUSH. The equation derived by the author (*Journal A. C. S.*, March, 1923) for rate of evaporation gives values for the rate of evaporation of electrons from tungsten molybdenum and titanium filaments at $2000^\circ K$. which agree closely with Langmuir's data. Dushman has derived an equation which probably gives even closer agreement with the experimental values, but which does not appear to allow for the existence of thermoelectric force. From the author's equation, with the aid of thermodynamics, a relation is derived between thermoelectric force and the rate of evaporation of electrons, and it appears possible to calculate the latter by measurement of the former at high temperatures. The assignment of specific heat to the conducting electrons in a metal appears to be an assumption not required by thermodynamics and contradicted by experimental evidence.

Absolute potential measurements: H. P. CADY AND GEORGE LYNN. The work was done by using a quadrant electrometer, one pair of quadrants being composed of mercury and the other the solution under investigation. The following is a summary of the results:

Trial No.	Method	Potential of Hg					
		Calomel			Hg ₂ SO ₄		
		Sat.	N/10 KCl	N KCl	N KCl	N/10 KCl	
1	Zero		— .157	— .283			
2	Deflec.		— .080				
3	Zero			— .170			
4	Deflec. (siphon)			— .212			
5	Deflec.	+ .150					
6	Deflec.	+ .175					
7	Deflec.	+ .215	+ .040	— .025			
8	Deflec.				+ .050		+ .097
9	Deflec.				— .200		— .160
10	Deflec.				— .085		— .047

None of the results approaches the value +.56 volts for the normal calomel electrode, but rather, with one exception, indicate that the mercury is negative to the solution and the values found for the N/10 calomel electrode agree fairly well with those published by Garrison.

A critical discussion of some generally accepted assumptions regarding cells with a liquid junction: GEORGE SCATCHARD. The proof of the elimination of liquid junction potentials by a saturated potassium chloride bridge, even the experimental proof, depends upon the assumption that the activities of the two ions of hydrochloric acid are equal. This assumption leads to considerable liquid junction potentials when the solvent is varied by increasing quantities of sucrose. The generally accepted formula for the electromotive force of a concentration cell with transport involves the assumption that the transport numbers are independent of the gradient of the ionic concentration. With sugar solutions this formula appears to give very erroneous results.

A comparison of electromotive force and freezing-point data: STUART J. BATES. By means of the following equation, the difference (ΔE) between the electromotive forces of cells, such as H₂, HCl (c), AgCl plus Ag, containing the electrolyte at different concentrations, may be calculated from the freezing-points of the solutions involved:

$$\frac{NF\lambda}{RT} \Delta E = \frac{(\theta_1 - \theta_2)}{(C_1 - C_2)} \quad \begin{array}{c} C_1 \\ \diagdown \\ C_2 \end{array} \quad \frac{\theta}{C} d \ln C.$$

For HCl observed values of ΔE for the concentrations 0.005 and 0.05 M are Noyes and Ellis 0.11248 volt, Linhart 0.1126. That calculated from the freezing-point data employing the "best values" of Noyes and Falk is 0.1146. For KCl for the same concentrations, MacInnes and Parker found 0.11085, the values calculated from different series of freezing-point measurements are Jahn 0.11190, Flugel 0.11178 and Adams 0.11207. If, on the other hand, the above equation be employed to calcu-

lated freezing-point lowerings from E. M. F. data, the difference between the observed and calculated values is again many times that which the precision of the measurements would indicate. The following equation was found to express the relation between activity coefficients (α) calculated from freezing-point data and the equivalent conductance ratio (Λ/Λ_0): $(1 - \alpha) = K(1 - \Lambda/\Lambda_0)$. By no means of this relation absolute values of activity coefficients may be calculated: these differ as a rule from those obtained by other methods. The above simple relation indicates that the factor or factors which operate in solution to decrease the equivalent conductance cause a proportional decrease in the activity coefficient.

The potential of the chlorine electrode in the presence of light: GRAHAM EDGAR AND J. A. MORROW. The potential of the chlorine electrode in hydrochloric acid solution has been measured in the dark and under intense illumination by the light of a quartz mercury arc. The light has no effect upon the potential within the limits of error of measurement (about 0.02 m.). This is interpreted to mean that light of the wave lengths employed can have no effect on the equilibrium between chlorine, hydrogen and hydrochloric acid gases. This is contrary to many views in the literature.

Luminescence among organo-magnesium halides: S. CALVERT, R. T. DUFFORD AND D. NIGHTINGALE. A study of over seventy Grignard compounds, of which over thirty were luminescent, reveals (1) that magnesium is necessary; (2) that ether is not; (3) that most aliphatics are inactive, while most aromatics are; (4) that substituents in the benzene ring affect the light (*a*) by their position, (*b*) by their chemical nature, (*c*) and not by their weight; (5) several very bright reactions are found, one, p. chlor. brom. magnesium benzene (MgC₆H₄ClBe), being probably the brightest on record. To give luminescence the Grignard must be derived from compounds containing halogen directly attached to unsaturated carbon.

The mechanism of the hydrogen-chloride combination: A. L. MARSHALL AND HUGH S. TAYLOR. An alternative method of testing Nernst's theory that the hydrogen-chlorine combination consists in the following sequence of reactions: $\text{Cl}_2 + \text{light} = \text{Cl} \cdot \text{Cl} \cdot$; $\text{Cl} \cdot + \text{H}_2 = \text{HCl} + \text{H} \cdot$; $\text{H} \cdot + \text{Cl}_2 = \text{HCl} + \text{Cl} \cdot$ consists in allowing a hydrogen chlorine mixture to flow into a vessel containing free hydrogen atoms. The experimental methods of securing this and the attempts to do this will be outlined.

Hydrogen, hydroxide and halide ions as inhibitors of photochemical reaction: W. T. ANDERSON, JR., AND H. S. TAYLOR. The inhibition of the photochemical decomposition of hydrogen peroxide by hydroxide and halide ions has been shown by a study of the velocity of decomposition of peroxide solutions containing these ions in amounts varied by addition of neutral salts.

The method of Willard Gibbs in chemical thermodynamics: W. LASH MILLER. In his treatment of the problems of chemical thermodynamics, Willard Gibbs postulated the two laws, invented what functions he needed to put them into form convenient for handling the problems presented by the laboratory, and developed equations for their solution which themselves suggest what experimental data must be supplied. The methods employed in current text-books of physical chemistry differ radically from that of Gibbs and are applicable only to artificially simplified problems; the reason usually advanced is the lack of suitable mathematical preparation on the part of students of chemistry. The customary elementary course on the calculus deals almost exclusively with explicit junctions of a single variable, while the physical chemist deals with functions of at least four independent variables, seldom presented in explicit form. Suggestions for modifying the customary course were made, which without adding to its length or its difficulty or detracting from its educative value, would make it applicable to the needs of chemists.

Interpretation of osmotic phenomena in terms of a modified form of the phase rule: A. S. McDANIEL.

The ammonia equilibrium: A. T. LARSON AND R. L. DODGE. The ammonia in equilibrium with $\text{N}_2 + 3\text{H}_2$ at pressures of 1, 10, 30, 50 and 100 atmospheres has been determined for the temperature range 300°—500°C. The experimental results obtained are in fair agreement with Haber's calculated values. It is shown that the equilibrium constant is not independent of the pressure, as has been assumed by earlier investigators, the differences increasing as the temperature is lowered.

The interpretation of time-temperature curves:

DONALD H. ANDREWS. A form of apparatus has been constructed such that the substance under observation loses heat at a rate proportional to the temperature difference between the substance and its surroundings. Under these circumstances the temperature of the substance can be expressed as a function of time, temperature head, the heat capacity and heat of fusion of the substance and the characteristics of the apparatus. In this way one can secure greater accuracy in the interpretation of the cooling curves of a binary or ternary mixture as compared with methods of interpretation which have been in general use.

Simplified construction of ternary freezing-point diagrams: G. T. KOHMAN. Several investigators have observed that certain binary and ternary systems, composed of ortho-meta-para isomers, behave substantially as ideal solutions. In the course of investigations of the thermal relation in such systems, it was noticed that this holds for all the cases which have been considered hitherto. This observation has resulted in the development of methods which enable one to construct the solubility diagram of this type of system from a small number of experimental determinations. These methods make it possible also to estimate very closely binary and ternary eutectic temperatures and compositions. Consequently they are of interest in view of the importance of solubility diagrams as a means of analyzing mixtures of ortho-meta-para isomers.

The system—silver perchlorate, aniline and water: ARTHUR E. HILL AND RUDOLPH V. MACY. The system has been studied from the eutectic (—57°) to plus 48°. The binary system silver perchlorate and aniline shows 4 compounds, respectively with 6, 3, 2 and 1 mol. of aniline to 1 of AgClO_4 . The compound $\text{AgClO}_4 \cdot 6 \text{An}$. is soluble in aniline to 5 per cent. at 25°, and melts congruently at 60.5°. The transition point to the 3-aniline compound is 48.3°; the later changes to the 2-aniline compound at 66.6°. The transition to the 1-aniline compound is above 100°, at which temperature oxidation of the aniline to nitrobenzene interferes. In the ternary system, the distribution of AgClO_4 between water and aniline is wholly in the aniline phase up to the point of saturation (9 per cent. AgClO_4). Both the 6-aniline and the 3-aniline compound are extremely insoluble in water; with excess aniline present, silver can not be detected in the water layer by addition of HCl, and with excess AgClO_4 present aniline can not be detected by Runge's test. Nine quintuple points have been found between —57 and plus 48°.

CHARLES L. PARSONS,
Secretary