

# ABSTRACTS OF THE PHYSICO-CHEMICAL LITERATURE IN JAPAN

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## 1—GENERAL AND PHYSICAL CHEMISTRY

1. **The equilibrium of the system aluminium sulphate—sulphuric acid—water at 25°C.**  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ ,  $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ . T. Motida. *J. Chem. Soc. Japan*, 58, 681-684 (1937).—In the equil. of the above system at 25°C there exists  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  solid phase in the range of sulphuric acid from zero to 7.24%. Another solid phase with  $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$  exists in the range between 7.81 and 48.13%. Author.

2. **Studies of hydrosulphite. VII. Reduction of bisulphite solution by sodium amalgam.** F. Ishikawa and N. Watanabe. *Bull. Inst. Phys. Chem. Research*, 16, 798-807 (1937).—The best yield (ca. 89%) of  $\text{Na}_2\text{S}_2\text{O}_4$  was obtained by reducing a properly diluted soln. of sodium bisulphite by sodium amalgam in a very diluted state. When a concd. soln. of  $\text{NaHSO}_3$  was used, a great quantity of  $\text{Na}_2\text{S}_2\text{O}_4$  produced crystallised out with  $\text{Na}_2\text{SO}_3$  from the soln., the solid phase having an approximate compn. of  $\text{Na}_2\text{S}_2\text{O}_4 + 3.5\text{Na}_2\text{SO}_3 + x\text{H}_2\text{O}$ . Authors.

3. **Some investigations on the photochemical methods for the measurement of ultraviolet radiation.** T. Imai. *Hokutsu Igk. Z.*, 52, 952-966 (1937).—Among the various photochem. methods for the measurement of ultraviolet radiation, the oxalic acid method (Anderson & Robinson) and the ammonium molybdate method (Hanzawa) were examd. The principal results of these expts. are as follows. 1. The decompn. of oxalic acid is almost proportional to the amt. of the radiation, while the reaction of the ammonium

molybdate becomes slower with prolonged exposure. This may be due to the fact that the transmission index of radiation in the oxalic acid soln. does not change throughout the process, while in the ammonium molybdate soln. it is decreased gradually with exposure.

2. For a const. exposed area the reaction value in a large quantity of soln. is greater, but the reaction value of unit volume in a large quantity of soln. is smaller because of the transmission index. In the oxalic acid method the ratio of the equiv. value for unit volume to the other is almost const., while in the ammonium molybdate method it approaches 1 with prolonged exposure. 3. The reaction is influenced slightly by the reflection factor of the substance under the soln. In the oxalic acid method the influence is almost const., while in the ammonium molybdate method it is reduced with the process of reaction. 4. Temp. has a slight influence on the reaction to almost the same extent in both methods. 5. Visible rays somewhat influence the reaction in both methods to a greater extent in the oxalic acid method. Author.

4. **The paramagnetic isomerisation of maleic acid into fumaric acid in aqueous solution.** B. Tamamushi and H. Akiyama. *Bull. Chem. Soc. Japan*, 12, 382-389 (1937).—The authors attempted to ascertain the possible catalytic influence of some paramagnetic substances,—such as molecular oxygen, Pt black and Pd black—and of some paramagnetic ions—such as  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Pr}^{3+}$ ,  $\text{Nd}^{3+}$  and  $\text{Er}^{3+}$ —on the isomerisation of maleic acid into fumaric acid in

aqueous soln. The exptl. results demonstrate that the isomerisation is more or less accelerated by the above catalysts, the isomerisation being probably effected by the non-homogeneous magnetic field of the catalysts in the collision. This is largely similar to the case where the para-ortho-hydrogen conversion in soln. could be accelerated by the presence of paramagnetic molecules and ions. The isomerisation of maleic acid into fumaric acid in aqueous soln. was kinetically studied both in the presence of paramagnetic  $O_2$  and in the presence of diamagnetic  $N_2$ , and the energy of the activation of the reaction was calcd. with the results:  $\ln k = 6.75 - (14600/RT)$  for  $O_2$ ,  $\ln k = 7.96 - (15800/RT)$  for  $N_2$ , where  $k$  is measured in sec. The lower energy of activation in the reaction with  $O_2$  may account for its catalytic effect. Authors.

5. On the deduction of the second law of thermodynamics. T. Yamaoka. *Proc. Phys.-Math. Soc. Japan*, III, 19, 246-249 (1937).—Since Carathéodory had clarified the relation between the phys. meaning of the second law and its mathematical representation and afterwards T. Ehrenfest-Afanasjewa had analysed the axiomatic structure of the principle, Planck reformed Carathéodory's deduction of the second law in such a way as to conform directly to the phys. facts which underlay the fundamental postulate. Now, from the phys. point of view, it seems desirable that the fundamental postulate should base itself on the experience of the simplest content, and the way of the deduction of the second law should be such that the axiomatic structure could be easily seen. In this short note an attempt has been made on this direction. Firstly, the starting postulate is "It is impossible to make a process completely reversible, in which heat is generated by friction". In this Planck's expression the one sided relation between the two forms of energy-mechanical work and heat is compactly contained. Secondly, the theorem on the integrability of the Pfaffian form is not used. In this way, the relation  $dQ = M dS$  is derived. The proof holds for the general systems. Author.

6. Spectroscopic studies on the reaction-flame. I. Reaction-flame of acetylene and halogens. H. Tominaga and G. Okamoto. *Bull. Chem. Soc. Japan*, 12, 401-404 (1937).—By means of analysis of spectrogramme of stable flame from acetylene and chlorine (bromine), a new type of chain-reaction was introduced.

II. Reaction-flame of mercury and halogens. *ibid.*, 404-408 (1937).—From a spectroscopic study of the flame formed by the reaction of mercury vapour and chlorine (bromine), the real existence of activated chlorine or bromine molecule in the flame was ascertained. Authors.

7. Studies on solubilities. IV. Solvency of mixed solvents I. S. Miyake and Y. Fukami. *Tech. Repts. Kyushu Imp. Univ.*, 12, 222-225 (1937).—Solubilities of salicylic acid in some mixed solvents obtained from pure benzene and a very small quantity of heavy water were studied at  $25^\circ C$  and compared with those values obtained with ordinary water. Solubility equilibria were obtained, without preheating (a), with preheating (b). The results are as follows:

## [I]

Heavy water (weight %)	Solubility	
	(a)	(b)
0	0.75	0.75
0.011	0.76	0.77
0.013	0.79	0.79
0.029	0.81	0.81
0.062	0.83	0.83
0.108	0.88	0.88
satd.	0.92	0.92
more than satd.	1.01	1.01

## [II]

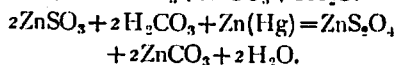
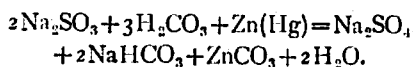
Water (weight %)	Solubility	
	(a)	(b)
0	0.75	0.75
0.027	0.85	—
0.039	0.89	—
0.046	0.92	—
more than satd.	1.01	1.01

Authors.

8. **Studies of hydrosulphite. VI. Reduction by zinc amalgam of solutions of sodium bisulphite.** H. Hagiisawa. *Bull. Inst. Phys. Chem. Research*, 16, 791-797 (1937).—Solns. of  $\text{NaHSO}_3$  in various concns. were reduced by zinc amalgam at  $10^\circ\text{C}$  under the action of one atmospheric carbon dioxide. The reaction  $4\text{NaHSO}_3 + \text{Zn(Hg)} = \text{Na}_2\text{S}_2\text{O}_4 + \text{ZnSO}_3 + \text{Na}_2\text{SO}_3 + 2\text{H}_2\text{O}$  proceeded completely, but the succeeding reaction  $\text{Na}_2\text{SO}_3 + \text{ZnSO}_3 + 2\text{H}_2\text{CO}_3 + \text{Zn(Hg)} = \text{Na}_2\text{S}_2\text{O}_4 + 2\text{ZnCO}_3 + 2\text{H}_2\text{O}$  proceeded unsatisfactorily. This may perhaps be due to the great concn. of  $\text{Na}_2\text{S}_2\text{O}_4$  produced by the first reaction. The compn. of the solid separated during the reduction may be represented by  $3\text{ZnCO}_3 \cdot \text{ZnSO}_3 \cdot 2\text{Na}_2\text{S}_2\text{O}_4$ . The difficulty in the second reaction was greatly reduced by increasing the press. of  $\text{CO}_2$  to ten atm. and shaking the soln. and the amalgam vigorously. Thus the yield in the second reaction could be increased to about 70%. Author.

9. **Studies of glass electrode and its applications. I.** K. Maruyama and H. Hagiisawa. *Bull. Inst. Phys. Chem. Research*, 16, 737-748 (1937).—Several glass electrodes of Haber's type were prepd. and their asymmetric potentials were measured by means of vacuum tube-potentiometer system designed by one of the present authors. The result was satisfactory, the asymmetric potential having been found to be about 0.5 mv. The titration of  $\text{H}_2\text{SO}_4$  in the presence of  $\text{KMnO}_4$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{KClO}_3$ ,  $\text{KBrO}_3$ ,  $\text{KIO}_3$ ,  $\text{CuSO}_4$  resp. and also the titrations of  $\text{HNO}_2$ ,  $\text{H}_2\text{Cr}_2\text{O}_7$ ,  $\text{H}_2\text{SO}_3$  were carried out with satisfactory results. Authors.

10. **Studies of hydrosulphite. V. Reduction by zinc amalgam of sodium sulphite and zinc sulphite under the action of carbon dioxide.** T. Murooka and H. Hagiisawa. *Bull. Inst. Phys. Chem. Research*, 16, 783-790 (1937).—Aqueous solns. of sodium sulphite and zinc sulphite could be reduced by zinc amalgam under the action of one atmospheric carbon dioxide, the reactions being represented by the following equations:



In each case the amts. of  $\text{Na}_2\text{S}_2\text{O}_4$  and  $\text{ZnS}_2\text{O}_4$  produced were detd. Owing to the small solubility  $\text{ZnSO}_3$  was more difficult to be reduced than  $\text{Na}_2\text{SO}_3$ , but reduction could be greatly increased by the use of satd. solns. (with solid salt) of  $\text{ZnSO}_3 \cdot 2.5\text{H}_2\text{O}$  in  $\text{Na}_2\text{SO}_3$  solns. of various concns. The reaction may be represented by the equation:  $\text{Na}_2\text{SO}_3 + \text{ZnSO}_3 + 2\text{H}_2\text{CO}_3 + \text{Zn(Hg)} = \text{Na}_2\text{S}_2\text{O}_4 + 2\text{ZnCO}_3 + 2\text{H}_2\text{O}$ . Authors.

11. **On the dissociation equilibrium of chromium nitrides.** K. Sano. *J. Chem. Soc. Japan*, 58, 981-984 (1937).—The dissocn. press. of chromium nitrides was measured by the statical method and the following relations were obtained.  $(\text{Cr}_2\text{N} = 2\text{Cr} + 1/2\text{N}_2) \log P_{\text{N}_2} = \frac{-9,558.311}{T} + 8.1034$ .  $(2\text{CrN} = \text{Cr}_2\text{N} + 1/2\text{N}_2) \log P_{\text{N}_2} = \frac{-12,071.25}{T} + 10.6546$ . From these results, some thermodynamical values were calcd. as follows:  $(2\text{Cr} + 1/2\text{N}_2 = \text{Cr}_2\text{N}) \Delta F_{298}^\circ = -17,262 \text{ cal}$ ,  $\Delta H_{298}^\circ = -20,602 \text{ cal}$ .  $(\text{Cr} + 1/2\text{N}_2 = \text{CrN}) \Delta F_{298}^\circ = -19,545 \text{ cal}$ ,  $\Delta H_{298}^\circ = -24,298 \text{ cal}$ . Author.

12. **The free energies of solution of zinc chloride and halides of cadmium.** F. Ishikawa and T. Takai. *Bull. Inst. Phys. Chem. Research*, 16, 1256-1261 (1937).—The differential and integral free energies of soln. and the differential free energy of dilution for the above-mentioned salts were obtained by measuring the electromotive force of reversible cells and the vapour press. of aqueous solns. of these salts. Authors.

13. **A study of symmetrical diethyl sulphite.** F. Ishikawa and C. Tanobe. *Bull. Inst. Phys. Chem. Research*, 16, 1318-1322 (1937).—The vapour pressures of  $\text{OS}(\text{OC}_2\text{H}_5)_2$  have been measured over the temp. range from  $0^\circ\text{C}$  to  $158^\circ\text{C}$  by the statical method using glass spring manometer as a zero instrument. The result may be represented by the following equation:

$$\log_{10} P_{(\text{mm})} = \frac{-2253.92}{T} + 1.75 \log T \\ - 0.001794 T + 4.272492.$$

From this result the heat of evaporation was calcd. as  $\lambda_{25^\circ} = 10623$  cal,  $\lambda_{157.8^\circ} = 10294$  cal (at boiling point). The values of Trouton const., Ramsay Shields const. and of parachor were discussed in relation to molecular association. The ester may be regarded as a normal liquid. The freezing point was detd. as  $-119.8^\circ$ . Authors.

14. **The integral free energies of solution of sodium chloride and potassium bromide.** F. Ishikawa and K. Moriwaki. *Bull. Inst. Phys. Chem. Research*, 16, 1244-1250 (1937).—The integral free energy of soln. of NaCl was calcd. by combining the result obtained by Allmand and Polack on the electromotive force of reversible cells with that obtained by Pearce and Nelson on the vapour press. of aqueous solns. The same energy for KBr was obtained by combining the result of vapour press. detn. with the differential free energy of soln. which had been detd. by F. Murata. Authors.

15. **The heat of formation and specific heat of vanadium nitride.** Shun-ichi Satoh. *Bull. Inst. Phys. Chem. Research*, 16, 1261-1269 (1937).—As the specific heat of vanadium nitride is not yet known, the mean specific heat of vanadium nitride was measured by the ice calorimeter for three temp. intervals:  $0^\circ\text{C}-99.6^\circ\text{C}$ ,  $0^\circ-305.3^\circ\text{C}$  and  $0^\circ\text{C}-458.6^\circ\text{C}$ , and the equation of the true specific heat was obtained:  $C = 0.1351 + 2.064 \times 10^{-4}t^2 - 1.057 \times 10^{-7}t^3$ . By using these values, the heat of formation of vanadium nitride was computed from the dissocn. press. of vanadium nitride at high temps. The result obtained is as follows:  $V + \frac{1}{2}N_2 = VN + 66,000$ . The relationship between the heat of formation of nitrides of the elements belonging to the 3rd series, 4th, 5th and 6th groups of the Periodic Table and their atomic numbers is discussed. Author.

16. **The partial pressure-rate of the**

**dry air.** K. Isihara. *Sea and Sky*, 17, 325-327 (1937).—To obtain the degree of satn. of dissolved oxygen in the sea or lake water, the vapour press. correction is to be applied for the solubility data such as those of Fox or Jacobson. When the barometer stands at 760 mm, Whipple and Whipple's table can be used, but in general we must take into consideration the value of  $\frac{P-f}{P}$  or  $1 - \frac{f}{P}$ , where  $P$  and  $f$  denote barometric press. and the vapour press. resp. The table of figures limited to the third decimals in the temp. range  $0^\circ\text{C}-30^\circ\text{C}$  and in the press. 600-780 mm is given for the purpose of practical use. Author.

17. **Chemical separation of heavy oxygen.** I. F. Ogawa. *Tech. Repts. Kyushu Imp. Univ.*, 12, 49-51 (1937).—The exchange reaction in which oxygen and nitrogen take part was examd., and the equil. consts. were calcd. by the Urey and Greiff method.

Reaction	Equil. Consts.
$\text{NO}_3^{18} + 3\text{H}_2\text{O}^{18} = \text{NO}_3^{16} + 3\text{H}_2\text{O}^{16}$	1.102
$\text{CrO}_4^{18} + 4\text{H}_2\text{O}^{18} = \text{CrO}_4^{16} + 4\text{H}_2\text{O}^{16}$	1.058
$\text{BrO}_3^{18} + 3\text{H}_2\text{O}^{18} = \text{BrO}_3^{16} + 3\text{H}_2\text{O}^{16}$	1.041
$\text{N}^{14}\text{H}_4\text{N}^{15}\text{O}_2 = \text{N}^{15}\text{H}_4 + \text{N}^{14}\text{O}$	1.006
$\text{N}^{14}\text{H}_4 + \text{CN}^{15} = \text{N}^{15}\text{H}_4 + \text{CN}^{14}$	1.0012
$2\text{N}^{15}\text{H}_4 + \text{N}_2^{14} = \text{N}_2^{15} + 2\text{N}^{14}\text{H}_4$	1.033

3 mol of each electrolyte— $\text{H}_2\text{O}$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{NaCl}$ ,  $\text{KCl}$ ,  $\text{CrCl}_3$ ,  $\text{CaCl}_2$ ,  $\text{BaCl}_2$ ,  $\text{CuCl}_2$ ,  $\text{NiCl}_2$ ,  $\text{FeCl}_3$ ,  $\text{KNO}_3$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{CuSO}_4$ ,  $\text{K}_3\text{Fe}(\text{CN})_6$ —was dissolved in 4 l of water, and it was distilled for 4 hrs. to 30 c.c. It was found that heavy oxygen could be thus conctd. J. C. L.

18. **Production of carbon monoxide and hydrogen by means of methane-steam reaction. II. Effect of hydrogen reduction temperature upon the catalytic activity of a nickel catalyst for the hydrogenation of benzene.** S. Tsutsumi. *J. Chem. Soc. Japan*, 58, 593-597 (1937).—The hydrogenation of benzene was examd. in the temp. range  $300^\circ-700^\circ\text{C}$  with a Ni catalyst mixed with 10% of various oxides as a catalyst promotor, and it was found that the yield of cyclohexane decreased with rising of temp.

The oxides prevented the catalytic activity from diminishing due to half-melting of the Ni catalyst, and  $\text{Al}_2\text{O}_3$  was more effective than any of  $\text{ThO}_2$ ,  $\text{SiO}_2$  and  $\text{MgO}$ .  $\text{MgO}$  lost the catalytic activity of reduction at  $500^\circ\text{C}$ , and  $\text{CaO}$  at  $400^\circ\text{C}$ .

**III. Action of a nickel catalyst upon methane-steam reaction.** *ibid.*, 58, 610-620 (1937).—The decompn. ratio of  $\text{CH}_4$  and  $(\text{CO}_2)/(\text{CO}+\text{CO}_2)$  were measured, varying the ratio  $\text{CH}_4:\text{H}_2\text{O}$  in the temp. range  $700^\circ\text{C}\sim 800^\circ\text{C}$  with the various catalyst promoters of Ni+10%  $\text{MgO}$ , and it was ascertained that Ni+10%  $\text{MgO}$  catalyst shows the max. activity. The mechanism of the reaction is considered comparing with those of the water-gas and thermal decompn. of methane.

**IV. Effect of nickel sulphate for a nickel catalyst.** *ibid.*, 58, 1007-1012 (1937).—The soln. of  $\text{Ni}(\text{NO}_3)_2+\text{Al}(\text{NO}_3)_3+\text{NiSO}_4$  was evaporated, dried and ignited below  $500^\circ\text{C}$ . The catalytic activity of this mass was diminished suddenly by a little addn. of  $\text{NiSO}_4$  for  $\text{CH}_4-\text{H}_2\text{O}$  reaction but not for  $\text{CO}-\text{H}_2\text{O}$  reaction. J. C. L.

**19. On the reaction between potassium chlorate and potassium iodide in a sulphuric acid solution.** K. Masuda. *J. Chem. Soc. Japan*, 58, 794-808 (1937).—Though the reaction represented by the equation  $\text{KClO}_3+3\text{H}_2\text{SO}_4+6\text{KI}=\text{KCl}+3\text{K}_2\text{SO}_4+3\text{H}_2\text{O}+3\text{I}_2$  has been detd. to be of the third order represented by (1)  $dx/dt=K_1(A-x)(B-x)(C-x)$ , the formula should be improved to be (2)  $dx/dt=K_2(A-x)(B-x)(C-\eta x)$ , where  $\eta$  may be regarded as the effective variation coeff. due to the reaction of KI. The reason is that generally  $\text{I}_2$  formed in such a reaction as  $\text{I}_2$  is septd. from KI produces molecular compounds by reacting on KI and removes these out of the reaction system.  $\eta=2$  was deduced from the measurement of reaction velocity, and  $K_2$  thus calcd. from (2) showed the far better const. value than  $K_1$  from (1). The above value of  $\eta$  is suitable from the solubility of  $\text{I}_2$  in KI soln. J. C. L.

**20. On the reducing action of amalgams.**

**VI. The mechanism of the interface reaction.** II. K. Masuda. *J. Chem. Soc. Japan*, 58, 873-882 (1937).—By varying the amt. of  $[\text{Zn}]$  in Zn-Hg between 2.0~0.05% and that of  $\text{H}_2\text{SO}_4$  between 0.0~2.0 N, the reducing power in the quiet state was measured. From the results obtained it was elucidated that the relation between  $\bar{Q}$ , the reacting quantity, and  $[\text{Zn}]$  in ZnHg and that between  $\bar{Q}$  and  $[\text{H}^+]$  of the soln. should be essentially represented by  $\bar{Q}=k(\text{Zn})^{-n}$  and  $\bar{Q}=a+b[\text{H}^+]$  resp. The relation in the reaction for a long hrs. became complicated, other elements being mixed. The reducing power was inverse proportion to concn. of the soln.

J. C. L.

**21. Electromagnetism in wave geometry.**

T. Iwatsuki, Y. Mimura and K. Morinaga. *J. Sci. Hiroshima Univ.*, A, 7, 255-257 (1937).—By classifying spin-parallelism deduced from the correspondence  $\psi'=(1+\sum)\psi\left[\sum^{(\omega)}=\left(\frac{x}{o}\middle|\frac{o}{x}\right)\right]$  between  $\psi$  and  $\psi'$  in two points in the space, the from  $\sum^{(\omega)}=\left(\frac{x}{o}\middle|\frac{o}{x}\right)$  causes the properties of gravitation and the form  $\sum^{(\omega)}\left(\frac{o}{x}\middle|\frac{x}{o}\right)$  the electromagnetic property. From this, the unified field theory can be realized in terms of wave geometry.

J. C. L.

**22. Exchange reaction of isotopes.** E. Ogawa. *J. Electrochem. Assoc.*, 5, 137-143 (1936).—The law stating that "the element in more pos. state is richer in heavier isotopes" was proved with respect to hydrogen and oxygen isotopes. Assuming that this law plays the important part in the exchange reaction of isotopes except those of hydrogen, it is stated that the production of  $\text{H}_2\text{O}^{18}$  is possible. Thus, from the assumption that the law is based on the difference of electron energy of isotope molecules, it is concluded that the theory stating that "the electron energies of isotope molecules are equal" is not general.

J. C. L.

**23. Action between neutron and proton.** Y. Nishina, S. Tomonaga and H. Tamaki,

*Sci. Papers Inst. Phys. Chem. Research*, 30, 61-65 (1936).—It is reported with the exptl. results that when the velocity of neutron decreases, its scattering due to collision with proton and the production of  $\gamma$ -rays increase. When the mutual action between neutron and proton is treated theoretically with the assumption that there coexist in the action the Heisenberg type and the Winger type, it is found that the scattering can be explained, but the theory of  $\gamma$ -rays does not coincide with the exptl. result. J. C. I.

24. **Studies on the action of a catalyst promotor and carrier. III. Selection of the catalyst for the synthesis of liquid hydrocarbons from carbon monoxide and hydrogen.** S. Tsutsumi. *J. Chem. Soc. Japan*, 58, 996-1001 (1937).—For a catalyst for hydrogenation of benzene, the activity of Ni with 10% promotors—MgO,  $\text{Al}_2\text{O}_3$ , CaO, CuO,  $\text{ThO}_2$ ,  $\text{Fe}_2\text{O}_3$ , MnO, ZnO and  $\text{SiO}_2$ —was compared with that of the catalyst with the add. of diatomaceous earth as a carrier, and it was found that (Ni+ $\text{Al}_2\text{O}_3$ )-catalyst kept its activity up to the higher temp. (700°C), but (Ni+CaO)-catalyst lost its catalytic activity at 400°C.

IV. **The activity of the catalyst for the synthesis of liquid hydrocarbons from carbon monoxide and hydrogen.** *ibid.*, 58, 1002-1006 (1937).—(Ni+10% $\text{Al}_2\text{O}_3$ )-catalyst for the synthesis of hydrocarbons from  $\text{CO}+\text{H}_2$  lost its catalytic activity even in the case where a little quantity of  $\text{NiSO}_4$  was added, but it keeps the power for the hydrogenation of benzene. J. C. I.

25. **Dipole moment and solvent. II. Electric moments of some amines.** K. Higasi. *Sci. Papers Inst. Phys. Chem. Research*, 31, 311-316 (1937).—The electric moments of diethyl and triethyl amines were measured in hexane and benzene solns., with the results:  $\text{N}(\text{C}_2\text{H}_5)_2$  1.10<sub>3</sub> D, 1.13<sub>1</sub> D, and  $\text{N}(\text{C}_2\text{H}_5)_3$  0.74<sub>9</sub> D, 0.78<sub>9</sub> D, resp. The moment in soln. increases with the increase in the dielectric const. of solvent. This tendency is also true when the data in vapour are taken

in consideration.

III. **Electric moment of di-isopropyl ketone.** K. Higasi. *ibid.*, 31, 317-320 (1937).—The apparent moment in soln. of di-isopropyl ketone were measured in benzene, hexane and carbon bisulphide soln. The results were compared with those in acetone. A neg. solvent effect was observed in spite of its neg. value in the Kerr const. Author.

26. **Raman effect and dipole moment in relation to free rotation. VII. Quantum mechanical resonance in carboxylic acid.** Y. Morino and S. Mizushima. *Sci. Papers Inst. Phys. Chem. Research*, 32, 33-43 (1937).—The Raman spectra of formic acid and sodium formate were studied. For the latter substance the result can be accounted for with the molecular model  $\text{H}-\text{C} \begin{smallmatrix} \diagup \text{O} \\ \diagdown \end{smallmatrix}$ , in which the two C—O links are equiv. because of the single bond double bond resonance. The values of force consts. calcd. from the observed frequencies are:  $k_{\text{CO}} = 9.29 \times 10^5$ ,  $k_{\text{CH}} = 4.27 \times 10^5$ , and  $(2d+d') \frac{S^2}{S_0^2} = 2.98 \times 10^5$  (dyne/cm.). The value of  $k_{\text{CO}}$  here obtained is nearly the mean value of those of single bond ( $5.0 \times 10^5$ ) and double bond ( $13.45 \times 10^5$ ). Authors.

27. **Raman effect and dipole moment in relation to free rotation. IX. Rotation around S-S bond.** Y. Morino and S. Mizushima. *Sci. Papers Inst. Phys. Chem. Research*, 32, 220-227 (1937).—The Raman spectra of sulphur monochloride  $\text{S}_2\text{Cl}_2$  were studied in liquid state and in carbon tetrachloride soln., and the dipole moment of this substance was measured in hexane soln. ( $\mu = 1.0$  D). It is concluded that the molecule of  $\text{S}_2\text{Cl}_2$  has the single bond structure  $\text{Cl}-\text{S}-\text{S}-\text{Cl}$ , the azimuth of one S-Cl group relative to the other being approximately 90°. Authors.

28. **Raman effect and dipole moment in relation to free rotation. VI.** K. Kozima and S. Mizushima. *Sci. Papers Inst. Phys. Chem. Research*, 31, 296-310 (1937).—The dipole moments of  $\text{CHBr}_2-\text{CHBr}_2$ ,  $\text{CCl}_2\text{Br}-\text{CCl}_2\text{Br}$ ,  $\text{o}-\text{C}_6\text{H}_4\text{ClOH}$ , and  $\text{o}-\text{C}_6\text{H}_4(\text{CH}_2$

$\text{Br}_2$  were studied in various solvents at different temps. The results are discussed in relation to the internal rotation of these molecules. The relative abundance of the two stable molecular species in the case of o-chlorophenol (due to quant. mech. resonance) is discussed from the temp. dependence of the dipole moment. Authors.

29. **Raman effect and dipole moment in relation to free rotation. VIII. Molecular structure of carbonic ester.** M. Kubo, Y. Morino and S. Mizushima. *Sci. Papers Inst. Phys. Chem. Research*, 32, 129-137 (1937).—The dipole moment  $\mu$  of dimethyl carbonate in vapour state was measured over a temp. range of  $150^\circ$  ( $\mu=0.86$  D at  $55.0^\circ\text{C}$ ,  $0.89$  D at  $76.9^\circ\text{C}$ ,  $0.94$  D at  $139.1^\circ\text{C}$ , and  $1.00_5$  D at  $206.2^\circ\text{C}$ ). The Raman spectra of dimethyl and diethyl carbonate were also studied. From these exptl. results the following conclusion is derived. The normal state of dimethyl carbonate can well be approximated by the classical formula  $\begin{array}{c} \text{CH}_3-\text{O} \\ \text{CH}_3-\text{O} \end{array} > \text{C}=\text{O}$ , so that there is no significant single bond-double bond resonance by which the internal configuration is linked rigidly. The molecule can, therefore, exert internal oscillatory rotation, the amplitude of which is easily affected by the change of temp.; i.e., there is an observable temp. dependence of dipole moment.

Authors.

30. **The reaction between ammonia and carbon dioxide.** T. Yoshida. *Kaken-Kōen-Shū*, 7, 213-223 (1937).—The influence of a trace of water vapour on the reaction  $\text{NH}_3\text{HCl}=\text{NH}_4\text{Cl}$  and its mechanism were investigated from the stand-point of chem. kinetics. While the reaction is stoichiometrically of the third order, it proceeds in reality as a reaction of the second order. And this reaction has a neg. temp. coeff. The following reaction mechanism is assumed: (a)  $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 \cdot \text{H}_2\text{O}$ , (b)  $\text{NH}_3 \cdot \text{H}_2\text{O} + \text{CO}_2 \rightleftharpoons \text{CO} < \begin{array}{c} \text{OH} \\ \text{NH}_2 \end{array} + \text{H}_2\text{O}$ , (c)  $\text{CO} < \begin{array}{c} \text{OH} \\ \text{NH}_2 \end{array} + \text{NH}_3 = \text{CO} < \begin{array}{c} \text{ONH}_2 \\ \text{NH}_2 \end{array}$ . From London's theory, taking E

as a seventh of Q,  $Q-E=6,523$  cal was obtained. The author's exptl. result coincides well with this calcd. value. J. C. L.

31. **On the optical properties of liquid mixtures of keton and alcohol. I—III.** T. Tomonari. *J. Soc. Chem. Ind. Japan*, 39, 577-588 (1937).—The appearance of a new intermolecular force between molecules of keton and alcohol by hydrogen ion was proved by the detn. of refraction and density. It leads to the formation of a keton-alcohol complex. J. C. L.

32. **Thermal analysis of engyme reactions. I. Invertase action.** T. Kōsaki. *This Journal*, 12, 21-46 (1938).

33. **Crystal structure of the aliphatic compound. III. The relation between specific gravity of a n-paraffin hydrocarbon and its properties.** R. Kobayashi. *J. Soc. Chem. Ind. Japan*, 40, 748-754 (1937).—The calcn. of the following points were made of various n-paraffin hydrocarbons: molecular diameter (D), molecular volume (V), molecular mass (S), melting point (F), sp. gr. at the melting point (S'), boiling point instability product and octane value. The calcd. values are compared with the measured ones, and the relation between them is elucidated. Exptl. results: (1) The linear relation  $S/S' = 0.2725 + 1.105 S$  holds between S and S'. As the value of S can be calcd. from the structure of molecule, the value of S' also can be obtained and it should coincide with the measured value. (2) The linear relation  $F = 587.5 S - 853.2$  holds between S and F. The calcd. value of F, generally, coincides with that of the melting point of n-paraffin hydrocarbon higher than n-butane. (3) Between B( $^\circ\text{K}$ ), the absolute boiling point, and S, the linear proportional relation  $\log (\log B) = 0.1329 S - 0.2393$  holds. The value of B calcd. from this equation should coincide with the measured one. (4) The linear proportional relation  $O_1 = 1.184 \cdot V/T^3 - 97.5$  holds between  $V(\text{\AA}^3)$ ,  $D(\text{\AA})$  and  $O_1$ , the octane value. (Here,  $V/T^3 = (D'/D) (D''/D) = a\beta\gamma$

and it denotes unstability product). The linear proportional relation  $O_2 = 1,131 \cdot M/D^3 - 118.7$  holds between  $M$ , molecular mass, and  $O_2$ , the octane value. (Here,  $M/D^3 = (M/V)(V/D^3) = S \cdot a\beta\gamma$  and it denotes product of molecular mass and unstability). As the octane value of

$n$ -paraffin hydrocarbons,  $O_2$  is applicable better than  $O_1$  represented in the above equation. Both values of  $O_1$  and  $O_2$  do not coincide with the octane values of paraffin hydrocarbons below  $n$ -butane.  
J. C. L.

## 2—ATOMIC STRUCTURE, RADIOCHEMISTRY AND PHOTOCHEMISTRY

34. The hydrogen atom in terms of wave geometry. K. Morinaga. *J. Sci. Hiroshima Univ.*, A, 7, 263-304 (1937).—Starting from the fundamental equation for  $\psi$  and assuming that it represents characteristic properties of atoms, the space was found to become necessarily spherical symmetric. Fij satisfies the Coulomb Law and  $\psi$  can be represented by the Whittaker  $W$  function.

J. C. L.

35. Chemical studies by means of molecular rays. IV. Proof of the primary photochemical decomposition of a diatomic molecule. E. Nishibori. *J. Chem. Soc. Japan*, 58, 4-13 (1937).—By introducing  $I_2$  molecular rays passing through a slit to a torsion balance of mica plate hung by quartz fibre,  $\Delta D/\Delta D$ , deviation, and  $D$  in the case where  $I_2$  molecular rays were illuminated by carbon arc were compared with those in the case where they were not illuminated. Thus, the photochem. decompn. of  $I_2$  was proved from the fact that  $\Delta D/D = 0.325 \pm 0.03\%$ , the measured value, agreed nearly with  $\Delta D/D = 0.269$ , the theoretical value, in the case where the photochem. decompn. of  $I_2 + h\nu \rightarrow I^* + I$  may be regarded to take place.

V. Direct determination of the effective radius of collision of the vibrationally excited iodine molecule with the mercury atom. *ibid.*, 14-21 (1937).—With the app. similar to that already reported, effective radius of  $I_2^*$ , previously excited vibrationally to the state of  $\Sigma$  by illumination, was compared with that of

ordinary  $I_2$  molecule for Hg atom.  $\sigma I_2^* = 5.72 \text{ \AA}$  was obtained, giving  $\sigma Hg = 1.82 \text{ \AA}$  and  $\sigma I_2 = 2.23 \text{ \AA}$ . From the comparison of the effective radius of the excited  $I_2^*$  for Hg with that of ordinary  $I_2$ ,  $5.72/2.23 = 2.56$  was obtained.

VI. Mass spectrographical investigation of the ions produced by the electron-bombardment of the molecular rays. *ibid.*, 22-36 (1936).—A kind of mass spectrograph was constructed, whereby the mass of molecular rays can be detd. They were ionized by the electron bombardment and the electric and the magnetic fields were made react on them. With  $I_2$  molecular rays several ions different in electric charges were thus detected.  
J. C. L.

36. Nuclear binding force. M. Nakabayashi. *Sci. Repts. Tohoku Imp. Univ.*, I, 25, 1141-1161 (1937).—With use of the wave equation of particle as the primary approximate value, the energy of binding of atomic nucleus was calcd. in the corresponding parabolic potential field. The exptl. err. calcd. as the secondary approximate value is corrected. The obtained value of energy is greater than that by the variation method.  
J. C. L.

37. On the energy of "residual neutrons." E. Takeda. *Proc. Phys.-Math. Soc. Japan*, III, 19, 393-394 (1937).—The expt. was performed mainly on the B-group neutrons using the residual neutrons from  $Be + Rn$  source (250 m Curie). The results obtained showed that the energy is distributed between



$10^5 \sim 10^4$  electron volts and a few electron volts. Similar expts. were made with iodine as a detector. J. C. L.

**38. New ultraviolet absorption bands of sodium and potassium molecules.**

H. Yoshinaga. *Proc. Phys.-Math. Soc. Japan*, **III**, **19**, 847-859 (1937).—New absorption bands found in this work, showed, when subjected to vibrational analysis, five systems for  $K_2$  molecule in the region between 4160 Å and 3480 Å and one system for  $Na_2$  molecule in the region between 2750 Å and 2550 Å. Occurrence of these bands is due to the transition from the normal state to the newly found states of each molecule. Close similarity is clearly seen among newly found  $K_2$  bands and  $Na_2$  and  $Li_2$  bands which were already observed in the ultra-violet region. Author.

**39. Classification of the near infra-red spectrum of mercury. II.**

O. Masaki and T. Morita. *J. Sci. Hiroshima Univ.*, **A**, **7**, 305-315 (1937).—In the authors' first paper with the same title, the near infra-red spectrum of Mg I to about 12000 Å was analysed by the photographic method. In the present research the mercury spectrum of the farther infra-red region, to about 14000 Å was photographed. The plates used for this expt. were Eastman I-Z plates, which were super-sensitized by the method of heat-treatment. Many new lines were found on the plate, the classification of which is given. Authors.

**40. An attempt to account for the Coulomb force between electron and proton.**

U. Kakinuma. *Proc. Phys.-Math. Soc. Japan*, **19**, 503-509 (1937).—The purpose of the present paper is to account for the Coulomb force acting between the electron and the proton by a hydrodynamical analogy. The idea is due to C. A. Bjerknes who made a thorough study of the electromagnetic phenomena from the hydrodynamical standpoint, by regarding the charged particles as pulsating spheres in an incompressible fluid. Although the study is very splendid in so far as the hydrodynamical phenomena are concerned, yet

there is a serious difficulty in its application to electrodynamics; viz. the spheres attract each other if their pulsations are in phase, and repel if they are in opposite phase. This seems to be the reverse in electricity and magnetism, where we have an attraction between unlike charges, and vice versa. But this situation may be saved if the notion of 'negative' length be admitted. According to the theory of the electron put forward by the author, the electron is a spherical entity of the smallest dimension (below  $10^{-30}$  cm). The proton may similarly be regarded as a spherical particle, the only difference from the electron being in the fact that the expression for the line element of the four-dimensional space associated with the proton is characterized by the introduction of *negative length*. This notion is considered to be more fundamental than that of *negative energy* and is an inevitable consequence of the existence of pos. and neg. electricity. With these slight modifications Bjerknes' idea has been revived in enabling us to interpret the Coulomb force satisfactorily with the aid of hydrodynamics.

Author.

**41. An attempt to interpret the observed stark effect in hydrogen molecule.**

M. Kiuti and H. Hasunuma. *Proc. Phys.-Math. Soc. Japan*, **III**, **19**, 821-834 (1937).—The authors attempt to obtain concordance of the observed Stark effect on molecular lines of hydrogen, which is apparently very complicated, with the theory. They employ their own observation newly, made and confine themselves to the triplet system. For the application of the theory, which is founded on mutual interactions between odd and even levels in the presence of the electric field, it requires accurate knowledge of the relative positions of the interacting levels. As the latter are as yet only roughly known, the authors determine them conversely by the examn. of the effect on the bands,  $3p^3\Sigma - 2s^3\Sigma$ ,  $2-0$  and  $3d^3\Delta_{u,1} - 2p^3\Pi$ ,  $0-0$ , for which the effect is mainly due to the lower terms. The relative positions are detd. thus with respect to the lower terms, and they are

verified by appearance of forbidden lines in the field. The result is that the level  $2p^3\Pi$  ( $v=0$ ,  $K=4$ ,  $a$ ) is to lie  $8.0\text{ cm}^{-1}$  higher than the level  $2s^3\Sigma$  ( $v=0$ ,  $K=3$ ,  $a$ ), from which all the required relative positions are known. With the relative positions thus detd., the effect on the 2-2 band of  $a$ , for which the upper terms are affected largely, may be well accounted for at least qualitatively. The authors, however, consider that the employed theoretical formula is not very adequate for the upper states but is still well applicable to the lower 2 quant. electronic states. Authors.

42. On the valence theory of the methane molecule. I. M. Kotani and M. Siga. *Proc. Phys.-Math. Soc. Japan*, 19, 471-486 (1937).—In order to examine the nature of the quadrivalent state of C atom and to investigate the degree of approximation of the assumption of electron pairing in Slater-Pauling theory of valency, energy of  $\text{CH}_4$  molecule was calcd. by Heitler-London's method, without assuming electron pair bond and taking C-atom configurations  $(2s)^2(2p)^2$ ,  $(2s)(2p)^3$  and  $(2p)^4$  into account. Making use of the tetrahedral symmetry of the molecule, the dimension of the secular equation is reduced to 7, but the numerical discussion is reserved for Part II. The same secular equation has been obtained independently by H. H. Voge, by a different method. Authors.

43. Note on the theory of electronic states of polyatomic molecules. M. Kotani. *Proc. Phys.-Math. Soc. Japan*, 19, 460-470 (1937).—Electronic terms of symmetric polyatomic molecules are classified according to the symmetry properties of their electronic wave functions, which are characterized by irreducible representations of certain crystallographic point-groups, as Mulliken has shown. In this paper the problem is treated, to determine the number of group-theoretically possible electronic terms of any polyatomic molecule, with the definite symmetry property and the definite spin multiplicity, when the angular momenta  $L$  and resultant spin  $S$  of the constituent atoms are given. Author.

44. On the energy states of valency electrons in some metals. I. 6. Some regularities existing in crystal level values and those of atomic spectrum of zinc. M. Satō. *Nippon Kinzoku Gakkai-Si*, 1, 161-164; *Sci. Repts. Tohoku Imp. Univ.*, I, 26, 206-213 (1937).—By studying the positions in energy of the crystal levels with respect to the optical terms of  $\text{ZnI}$ , the following regularities were found:—Depression;  $E_1 - (4s)^2 {}^1S_0 = (4s, 4p)^3 P_0 - (4s, 5p)^3 P_1$ . Depression;  $E_2 - (4s)^2 {}^1S_0 = (4s, 4p)^1 P_1 - (4s, 4d)^1 D_2$ . Elevation;  $(4s)^2 {}^1S_0 - E_3 = (4s, 5p)^1 P_1 - (4s, 9p)^1 P_1$ . Elevation;  $(4s)^2 {}^1S_0 - E_4 = (4s, 5p)^3 P_1 - (4s, 9d)^3 D$ . From these results the following configurations of electrons for the crystal levels were assigned:  $E_1(4s, 4p; 4s, 5p)$ ,  $E_2(4s, 4p; 4s, 4d)$ ,  $E_3(4s, 5p; 4s, 9p)$ ,  $E_4(4s, 5p; 4s, 9d)$ . Author.

45. Molecular spectra of zinc hydride and deuteride. Y. Fujioka and Y. Tanaka. *Sci. Papers Inst. Phys. Chem. Research*, 32, 143-156 (1937).—The  ${}^2\Pi \rightarrow {}^2\Sigma$  bands of  $\text{ZnH}$  and  $\text{ZnD}$  in the violet region are photographed with the use of a 6-meter concave grating in the second order. In each case, twelve branches of  $o \rightarrow o$  bands are analysed and the consts. of  ${}^2\Sigma$  and  ${}^2\Pi$  states are calcd. As the vibrational levels are not observed at all, the consts. of the electronic states ( $\text{Be}$ ,  $\text{De}$  etc.) are not calcd. It is difficult, therefore, to discuss precisely the isotope effect. Authors.

46. The third absorption bands of Co-ordination compounds. IV.  $[\text{Codg}'\cdot\text{pyCl}]$ ,  $[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_2\text{ox}][\text{NH}_4\cdot\text{H}_2\text{O}]$  and  $[\text{Co ox}_3]\text{K}_3\cdot 3.5\text{H}_2\text{O}$ . S. Kashimoto and M. Kobayashi. *Bull. Chem. Soc. Japan*, 12, 350-352 (1937).—According to Y. Shibata and R. Tsuchida, the third absorption bands of co-ordination compds. are due to a pair or pairs of neg. radicals co-ordinated in transposition to each other. To substantiate this postulate extinction-coeffs. of  $[\text{Codg}'\cdot\text{pyCl}]$ ,  $[\text{Co}(\text{NH}_3)_2(\text{NO}_2)_2\text{ox}][\text{NH}_4\cdot\text{H}_2\text{O}]$  and  $[\text{Co ox}_3]\text{K}_3\cdot 3.5\text{H}_2\text{O}$  were measured. Aqueous solns. of these salts were proved to have the third absorption bands.

Authors.

47. **On the reversal temperature of the system containing sodium and potassium.** H. Yoshinaga. *Proc. Phys.-Math. Soc. Japan*, III, 19, 386-392 (1937).—The study of the spectrum emitted by a vacuum arc contg. sodium and potassium shows that the reversal temp. of the spectral line of the sharp and diffuse series of these elements is quite the same irrespective of the difference in series or of the difference in elements. Accordingly, we can obtain the relation between the concn. of normal atoms of these elements in a light source and the intensity ratio of any spectral lines of the sharp and diffuse series of both elements, by determining the reversal temp. by the intensity measurement.

Author.

48. **The absorption spectra of metallic complex salts of 2,2'-dipyridyl.** I. K. Yamasaki. *Bull. Chem. Soc. Japan*, 12, 390-394 (1937).—The absorption spectra of aqueous and alcoholic soln. of tri[dipyridyl] complex salts of Cu, Zn, Ni, Fe and Co were studied at room temp. as well as at low temp. ( $-60^{\circ}\text{C} \sim -70^{\circ}\text{C}$ ).

Author.

49. **On the number of quanta of gamma-rays emitted from a nucleus when it captures a neutron.** H. Aoki. *Proc. Phys.-Math. Soc. Japan*, III, 19, 799-805 (1937).—Using the method of coincidence of two Geiger-Müller counters, the mean number of gamma-ray quanta emitted from a nucleus when it captures a neutron was estimated. It was found that several quanta of gamma-rays are frequently emitted by a capture process.

J. C. L.

50. **On hard gamma-rays from  $\text{Ra}(\text{C} + \text{C}' + \text{D})$ .** S. Nishida. *Proc. Phys.-Math. Soc. Japan*, III, 19, 809-817 (1937).—The results of the observation of electron tracks of the hard gamma-rays in a Wilson chamber showed that the hardness of the gamma-rays was about  $3.1$ ,  $4$  and  $4.9 \times 10^6$  e.v. Therefore, it is certain that such an abnormal betadecay-phenomenon as remarked by Rutherford and others cannot be expected. After considering

carefully the energy relations of  $\text{RaC}$  by products, it is concluded that these hard gamma-rays are due to the emissions from  $\text{RaC}'$ — $\text{RaD}$ . The energy-diagram between  $\text{RaC}$  and  $\text{RaD}$  is constructed.

J. C. L.

51. **New foundation of atomic structure.** Y. Mimura and T. Iwatsuki. *J. Sci. Hiroshima Univ.*, A, 7, 259-261 (1937).—From the standpoint of the field theory it is assumed by adopting the Einstein theory on solar system that the atomic structure is in itself the structure of space-time due to the nucleus.

J. C. L.

52. **Disintegration of nucleus by cosmic radiation.** S. Nishida. *Proc. Phys.-Math. Soc. Japan*, III, 19, 818-820 (1937).—In the course of the exptl. work using a Wilson chamber, dense tracks showing the explosions of atomic nuclei by cosmic radiation were observed. The angle between the two tracks was slightly less than  $2\pi$ . As the chamber contained air of one atmospheric pressure and ethyl alcohol, the disintegrated nucleus must have been one of C, N and O. To estimate the order of the in-coming ray, it is possible to consider the following reaction process:  ${}_6\text{C}^{12} \rightarrow {}_3\text{Li}^5 + {}_3\text{Li}^6 + {}_0\text{n}'$ .

J. C. L.

53. **The cathode-luminescence spectra of feldspars and other alkali aluminosilicate minerals.** S. Iimori and J. Yoshimura. *Sci. Papers. Inst. Phys. Chem. Research*, 31, 281-295 (1937).—Feldspars from four different localities were employed as samples. It was found that all of these specimens were strongly luminescent but the colour of luminescence was slightly different one from another and that their spectra consisted in general of three broadened bands. Comparing these spectra with those of other alkali aluminosilicate minerals, the influence of various micro-components upon intensity of the spectra is discussed.

J. C. L.

54. **On the energy states of valency electrons in some metals. 1.8. Calculation of the heat of sublimation of zinc**

from the differences between its crystal energy levels and atomic normal level. Mituru Satō. *Nippon Kinzoku Gakkai-Si*, I, 248-250 (1937).—From the differences between the energy values of the crystal levels of zinc and that of the normal state of Zn-atom, the heat of sublimation of solid-Zn was calcd. to be 0.099 Ryd. per atom, which is in perfect agreement with the exptl. value, 0.098 Ryd. per atom.

Author.

55. On the energy states of valency electrons in some metals. 1.7. The emission and absorption of X-rays in zinc and zinc oxide, relating to the outer levels of Zn. Mituru Satō. *Nippon Kinzoku Gakkai-Si*, I, 232-247 (1937).—The nature of the phenomena of K-absorption of X-ray by zinc was investigated and it was found that the phenomena consist of a main process and an auxiliary one. The former is the electron transition from k-shell or the level,  $(1s)^2 1S_0$ , to the optical level,  $(4s, 4p)^1P_1$ , ZnI, resulting in the so-called K-absorption main edge. The latter, in nature, is Auger effect, giving rise to some breadth to the K-absorption edge, the emission lines,  $K\beta_2$  and  $K\beta'''$ , and to a fine structure of the main edge itself. The nature of L-absorption of X-ray by zinc was also studied and it was found that the main process is the electron transition from  $L_{II, III}$  to the optical level of the triplet system of ZnI,  $(4s, 6s)^3S_1$ , and the auxiliary one is the electron transitions between the levels, belonging to the triplet system of ZnI. K- and  $L_{II, III}$ -absorptions in zinc oxide are also described. In these cases, the main processes are the same as in the cases of zinc resp., but the auxiliary ones consist of the electron transitions between atomic levels of oxygen of ZnO; this causes the shifting of the absorption edges.

Author.

56. The light absorption of silver halides and their photographic sensitivity. N. Kameyama and S. Kikuchi. *J. Soc. Chem. Ind. Japan*, 40, 858-860 (1937).—The energy necessary to photochem. decompn. was calcd. from the electron affinity

of halogen ions, the ionization energy of silver atom, the crystal lattice energy and the energy of adsorption of bromine and silver atoms to the crystal. 325 m $\mu$  and 410 m $\mu$  were obtained for silver chloride and silver bromide resp. These two values are approximate to 390 m $\mu$  for silver chloride and to 435~480 m $\mu$  for silver bromide, the values of actually sensitive long wave ends. The calcn. is made for the perfect crystal but the real crystal is usually imperfect, and the sensitivity should take place with slightly less energy than that of calcd. value.

J. C. L.

57. On the spectrum of silicon. T. Takamine, T. Suga, and M. Kamiyama. *Sci. Papers Inst. Phys. Chem. Research*, 33, 247-271 (1937).—When a strong condensed discharge is passed through a fine quartz capillary in hydrogen at low press., silicon spectra at successive stages of ionization are seen superposed on the Lyman continuum. The extreme ultra-violet part of these spectra was studied by means of a vacuum spectrograph having a 1 metre concave grating at grazing incidence. Special features observed were the changing of many of the SiI and SiII lines from emission to absorption as the energy of the spark was increased. Especially interesting was the marked difference in the degree of easiness for reversal seen for different SiII lines. Lines of SiIII and SiIV came out mostly in emission. Relation between the stellar temp. classification and the temp. in the light source used in laboratory expt. is discussed.

Authors.

58. On the positive ion emission from heated nickel wire in oxygen and hydrogen. R. Goto. *Proc. Imp. Acad.*, 13, 320-324 (1937); *This Journal*, 12, 15-20 (1938).

59. A study of the new bands of SiF. T. Yuasa. *Sci. Repts. Tokyo Bunrika Dai-gaku*, A, 3, 195-203 (1937).—In the region of the wave-lengths between 6680 Å and 3100 Å, the author found three systems of new bands, i.e.  $\lambda\lambda 3839.757 \text{ Å} \sim 3293.079 \text{ Å}$  (degraded to-

wards red),  $\lambda\lambda$  3413.757 Å~3244.71 Å (degraded toward violet) and  $\lambda\lambda$  3365.83 Å~3198.77 Å (degraded towards red). These bands are considered to belong to SiF. The wave-lengths of the heads of these bands were measured by taking the photograph of the spectrum with Hilger's El. The vibrational analysis of the first system ( $\lambda\lambda$  3839.052 Å~3293.079 Å) was made, and it was found that the lower level of this system is the same as the ground level of the molecule SiF as decided by a previous author. The molecular consts. of the levels,  $x_e$ ,  $r_e$  and  $x_v$ , are calcd. to be 4.1 cm<sup>-1</sup> and 911.2 cm<sup>-1</sup> for the higher and 4.3 cm<sup>-1</sup> and 858.6 cm<sup>-1</sup> for the lower.

Author.

60. On the binding energy of atomic nuclei. II. T. Yamanouchi. *Proc. Phys.-Math. Soc. Japan*, III, 19, 790-797 (1937).—The difference of proton and neutron is studied by applying the author's theory already reported (See this Journal, 11, 227 (1937)).—The value represented by the formula contg. a few parameters is hard to be calcd., but by eliminating these parameters the relation of mass defect among various atomic nuclei is obtained. The

value coincides nearly with that of the expt.

J. C. L.

61. Isotope displacement in tungsten lines. M. Kiuti, H. Hasunuma and T. Kawada. *Proc. Phys.-Math. Soc. Japan*, III, 19, 1019-1022 (1937).—Fine structure of W spectrum lines in the visible and the ultraviolet regions was studied by using a Fabry-Perot interferometer and a quartz Lummer plate. The authors found some terms which show larger displacement than the standard terms 5d<sup>4</sup>6s<sup>2</sup>D.

J. C. L.

62. Abnormal specific heat of ammonium chloride crystal with substituted heavy hydrogen. I. Nitta and K. Suenaga. *Sci. Papers Inst. Phys. Chem. Research*, 32, 83-86 (1937).—The transition phenomenon assumed to be due to the rotation of ammonium ion in the crystal was studied with the crystal of ND<sub>4</sub>Cl. The sp. heat of 92.5% ND<sub>4</sub>Cl crystal obtained by the exchange reaction between D<sub>2</sub>O and NH<sub>4</sub>Cl was measured in the temp. range—170°C~50°C by a vacuum calorimeter. It was found that the transition similar to that of NH<sub>4</sub>Cl at -30.4°C took place at -24°C.

J. C. L.

### 3—ELECTROCHEMISTRY AND THERMOCHEMISTRY

63. Researches on the electric boundary layer disturbance. XII. The absorption of electromagnetic waves at high temperatures by the dispersed system of particles of cellulosic substance. II. M. Shikata and S. Ueda. *J. Electrochem. Assoc. Japan*, 5, 298-306 (1937).—In order to study the state of water absorbed by  $\alpha$ -cellulose, the absorption of electromagnetic waves with frequencies less than 6,000~ has been measured at 30°C~100°C with system Solka  $\alpha$ -flock-liquid paraffin, the water content of the system being less than 8%. Solka  $\alpha$ -flock, the preparation of American Brown Co., contg. over 98%  $\alpha$ -cellulose, was used in 100- and 200-mesh finesses. The results obtained

are summarized as follows: when the temp. is raised, the dielectric loss appears in ranges of lower frequencies; if the frequency is the same, the dielectric loss is observed in scopes of lower water content with the rising temp. The max. dielectric loss occurs, when the acting frequency is altered, and the frequency corresponding hereto moved to regions of higher frequencies and the magnitude of max. is increased as the water content and the temp. are increased. The characteristic trend of the relaxation time calcd. from the exptl. results is in good agreement with the theoretical calcn., i.e., the value of  $\tau$  decreases with the increase in the water content and the rise in the temp.

Authors.

64. **The heat of formation and specific heat of aluminium carbide.** S. Satoh. *Bull. Inst. Phys.-Chem. Research*, **16**, 757-764 (1937).—The mean specific heat of aluminum carbide was measured by the ice calorimeter for three temp. intervals:  $0^{\circ}\text{C}\sim 99.6^{\circ}\text{C}$ ,  $0^{\circ}\text{C}\sim 244^{\circ}\text{C}$  and  $0^{\circ}\sim 320.5^{\circ}\text{C}$ , and the equation of the true specific heat was obtained:  $C=0.2282+2.12\times 10^{-4}t-2.842\times 10^{-8}t^2$ . By using these data, the heat of formation of aluminium carbide was computed taking into consideration the formation of the aluminium carbonitride from the equil. data of the reaction  $4\text{AlN}+3\text{C}=\text{Al}_4\text{C}_3+2\text{N}_2$ , at high temps. The result obtained is as follows:  $4\text{Al}+3\text{C}=\text{Al}_4\text{C}_3+63200\text{ cal.}$  Author.

65. **Diffusion of strong electrolytes and individual activity coefficients of ions.** S. Kaneko. *J. Chem. Soc. Japan*, **58**, 790-793 (1937).—The author modified his former reports on diffusion of strong electrolytes and individual activity coeff. of ions [*ibid.* **56**, 1322 (1935); **57**, 11 and 307 (1936)], thus removing some inconsistency therein and perfecting his theory. Author.

66. **The heat of formation and specific heat of nilicon nitride.** Shun-ichi Satoh. *Bull. Inst. Phys. Chem. Research*, **16**, 906-914 (1937).—Since the specific heat of silicon nitride is not known, the mean specific heat of silicon nitride was measured by the ice calorimeter for three temp. intervals:  $0^{\circ}\text{C}\sim 99.5^{\circ}\text{C}$ ,  $0^{\circ}\text{C}\sim 316.4^{\circ}\text{C}$  and  $0^{\circ}\text{C}\sim 585^{\circ}\text{C}$ , and the equation of the true specific heat was obtained:  $C=0.1656+1.847\times 10^{-4}t-4.5\times 10^{-8}t^2$ . By using these values, the heat of formation of silicon nitride was computed from the disson. press. of silicon nitride at high temps. The result obtained is as follows:  $3\text{Si}+2\text{N}_2=\text{Si}_3\text{N}_4+163,000$ . The relationship between the heat of formation of nitrides of the elements belonging to the 2nd serie of the Periodic Table of the elements and their atomic numbers is discussed. Author.

67. **On the solubility and the dissociation of lead chloride in solutions of**

**potassium nitrate.** F. Ishikawa and K. Moriaki. *Bull. Inst. Phys. Chem. Research*, **16**, 915-920 (1937).—The solubility of  $\text{PbCl}_2$  in aqueous solns. of  $\text{KNO}_3$  was measured at  $25^{\circ}\text{C}$ . Debye-Hückel and Hückel equations were applied to the result assuming a complete disson. of  $\text{PbCl}_2$ . The latter equation was found to be applicable to this case. The disson. of  $\text{PbCl}_2$  in two stages was theoretically treated as had been done by MacDougall and Hoffman in the case of  $\text{Pb}(\text{BrO}_3)_2$ , and the result was obtained which seemed to be favourable to this kind of disson. Authors.

68. **Equivalent conductivity and transport. Number of 1-1 salts.** S. Kaneko. *J. Chem. Soc. Japan*, **58**, 985-988 (1937).—By means of the formula derived in the former report (*Researches Electrotech. Lab.*, **403**, "Extension of Debye-Hückel's theory of strong electrolytes") equiv. conductivity and transport number of 1-1 salts are calcd. and compared with the measurement of Shedrovsky. By the assumption of reasonable size of ions the calcd. and observed values coincide remarkably well. Author.

69. **Studies on fluorine at low temperatures. I. Preparation, analysis and handling of fluorine.** S. Aoyama and F. Kanda. *J. Chem. Soc. Japan*, **58**, 706-710 (1937); *Bull. Chem. Soc. Japan*, **12**, 409-416 (1937).—By improving Dennis' V-shaped app. for electrolysis, fluorine was prepd. from molten acid potassium fluoride. The yield was 75-90%, and the fluorine was kept in the liquid state in a glass trap cooled by nitrogen. For the quantitative detn., fluorine was shaken with small granules of mercury to from mercury fluoride. Cu, Mg, Ni, and monel-metal were suitable as the materials for the app. of examg. the properties of fluorine. Discussion is given of gas-tight materials and vacuum corks. Results of the expts. concerning the combustion of charcoal, phosphorus, silicon, tellurium and selenium in fluorine gas at ordinary temp. are also given.

**II. Vapour pressure of fluorine.** *ibid.*, **12**, 416-419 (1937).—The vapour press.

of liquid and solid fluorine was measured in the temp. range  $51.85^{\circ}\text{K} \sim 86.21^{\circ}\text{K}$  by the platinum film press. gauge. The vapour press. of liquid fluorine can be represented as follows:  $\log P_{\text{mm}} = -442.72/T + 9.1975 - 0.013150 T$ . The boiling point of fluorine and its calcd. heat of vaporization were detd. to be  $85.19^{\circ}\text{K}$  and 1,581 cal. resp.

**III. Solution of chlorine in liquid fluorine.** *ibid.*, 12, 455-457 (1937).—A small quantity of chlorine could be dissolved in liquid fluorine. Sometimes traces of chlorine could be found in liquid fluorine formed by the method reported in I. The quantity of chlorine in the soln. satd. at  $-195^{\circ}\text{C}$  was 1.04%. A special app. was devised for the quantitative detn. of crystals dissolved in a liquified permanent gas.

**IV. Separation of fluorine from oxygen by adsorption and rectification.** E. Kanda. *J. Chem. Soc. Japan*, 58, 804-809 (1937); *Bull. Chem. Soc. Japan*, 12, 463-468 (1937).—On account of the fact that oxygen and fluorine are very similar to each other in respects of methods of prepn., molecular weights and boiling points, mixing of oxygen with fluorine is unavoidable, and it is difficult to remove oxygen from fluorine with chem. reagents requiring low temp. in their handling. Employing a quartz spring balance, adsorption of fluorine on active carbon was compared with that of hydrogen under various press. in temp. range  $0^{\circ}\text{C} \sim -183^{\circ}\text{C}$ , and it was found that hydrogen was adsorbed in a greater quantity than fluorine. Applying this phenomenon to the prepn. of fluorine, 99.4%  $\text{F}_2$  was produced from a mixt. of 96%  $\text{F}_2 + 3.7\% \text{O}_2$ . As boiling points of fluorine and of oxygen are  $-188^{\circ}\text{C}$  and  $-183^{\circ}\text{C}$  resp., it is hard to separate fluorine from oxygen only by fractional distillation, but with the refining app. 99% pure fluorine could be obtained from an original liquid contg. 95% fluorine.

**V. Viscosity of fluorine gas at low temperatures.** E. Kanda. *J. Chem. Soc. Japan*, 58, 804-809 (1937); *Bull. Chem. Soc. Japan*, 12, 463-468 (1937).—By measuring the decrement ratio of the rotational oscillation of a disc., the viscosity coeff. ( $\eta$ ) of fluorine

gas was measured in the temp. range  $0^{\circ}\text{C} \sim -186.4^{\circ}\text{C}$ . The two values,  $\eta(0^{\circ}\text{C}) = 2.093 \times 10^{-7}$  and  $\eta(-186.4^{\circ}\text{C}) = 555 \times 10^{-7}$ , and the intervening values were obtained. From the values of  $\eta$ , Sutherland's const.,  $C = 129$ , of fluorine can be obtained. The diameter of the molecule and the mean free path were measured to be  $d = 3.02 \text{ \AA}$  and  $L = 9.12 \times 10^{-6} \text{ cm}$  resp.

**VI. Surface tension of liquid fluorine.** *ibid.*, 12, 469-472 (1937).—The surface tension ( $\gamma$ ) of liquid hydrogen and liquid fluorine was detd. by the method of capillary tube. The following results were obtained with respect to liquid fluorine.

Temp.	64.41	65.30	71.00	81.50°K
$\gamma$	13.85	13.17	12.20	10.41

Liquid fluorine may be regarded as a normal liquid, conforming practically with Eötvös' law.

**VII. Dielectric constant of some condensed gases.** E. Kanda. *J. Chem. Soc. Japan*, 58, 857-864 (1937); *Bull. Chem. Soc. Japan*, 12, 473-479 (1937).—Dielectric consts. of liquid oxygen, fluorine, chlorine and hydrogen chloride in the electric field of frequency were measured by "Beat method". Various apps. for keeping const. temp. were devised, as the temp. ranged between  $57.4^{\circ}\text{K}$  and  $239^{\circ}\text{K}$ , and, especially, for  $-195^{\circ}\text{C} \sim 250^{\circ}\text{C}$ , a cryostat with vapour of liquid hydrogen was used as cooling medium. While the dielectric const. was detd., the density of the above four condensed gases were measured. From the results obtained the molecular polarization at each temp. was detd., and it was found that oxygen, fluorine and chlorine are of non-polar, and that hydrogen chloride shows abnormality in the solid state owing to the inner molecular rotation.

**VIII. Determination of molecular heat, heat of fusion of condensed fluorine and the entropy of fluorine.** E. Kanda. *Bull. Chem. Soc. Japan*, 12, 511-520 (1937).—The app. for obtaining given const. temp. in the temp. range  $80^{\circ}\text{K} \sim 15^{\circ}\text{K}$  was devised, and especially temps. between  $20^{\circ}\text{K}$  and  $15^{\circ}\text{K}$  were detd. by employing the temp. near F. P. of liquid hydrogen. Thus

the specific heat of solid hydrogen was measured to be 24.2°K, 42.9°K and 54.3°K at the transition points, I, II and M. P. resp. As for fluorine, M.P. 55.2°K and B.P. 85.19°K were obtained, and the molecular heat below 20°K conformed nearly to the  $T^3$  law by Debye. Characteristic temp. was found to be  $\theta = 100.3$ . From the values of molecular heat and heat of fusion, 37.29 (entropy unit) was obtained as the entropy of fluorine vapour.

**IX. Experiment on the reaction between solid fluorine and liquid hydrogen.** S. Aoyama and E. Kanda. *J. Chem. Soc. Japan*, 58, 871-872 (1937); *Bull. Chem. Soc. Japan*, 12, 511-524 (1937).—Since Dewar and Moissan reported that explosion took place at  $-252^\circ$  when solid fluorine was put into contact with hydrogen, the cause of the explosion has been ascribed to contamination of some org. substances. Under necessary precautions of expts., solid fluorine was put into contact with liquid hydrogen, and an explosive reaction was found to take place between them. Various possible causes of the explosive reaction are considered.

J. C. I.

**70. The electrolytic formation of persulphate. IV. Influence of temperature.** R. Matuda, H. Konya and T. Nishimori. *Bull. Chem. Soc. Japan*, 12, 425-432 (1937).—7 N ammonium sulphate soln. and 10, 15, 20, 25, 30, and 36 N sulphuric acid are electrolysed at 5°C, 15°C and 25°C. without diaphragm. In ammonium sulphate soln. and 10 N and 15 N  $H_2SO_4$ , only a small quantity of Caro's acid was formed, the current efficiency of formation of persulphate increasing with lowering of temp. or with increase of current density (5~80 Amp./dm.<sup>2</sup>). In the concd. sulphuric acid over 20 N, however, Caro's acid occupied greater part of the product showing the max. of the current efficiency at the current density 10~30 Amp./dm.<sup>2</sup>. The mechanism of the formation of persulphuric acid is discussed with the view that persulphuric acid is formed by the oxidation of sulphuric acid with the anodic oxygen and

not by discharge polymerization of  $HSO_4'$ .  
J. C. I.

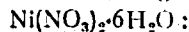
**71. Ion sheath.** Y. Watanabe and M. Aoyama. *J. Inst. Elec. Eng. Japan*, 57, 915-921 (1937).—Ion current and press. were observed in the case where the thickness of ion sheath ranged from a few mm to a few cm, and it was ascertained that Langmuir's law held well. Phys. considerations are given of the numerical values of ion current density and ion density.  
J. C. I.

**72. On the hydrogen peroxide electrode.** K. Kodama and T. Onizuka. *J. Biochem.*, 25, 573-578 (1937).—Using the  $H_2O_2$ -electrode the relation between the potential (m.v.) and the activity of H-ion in various buffer mixts. at 20°C can be represented by the equation  $E = E_0 - 51.8 \times pH$ , and some theoretical discussion for this equation are given.

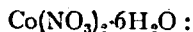
Authors.

**73. Electric discharge.** S. Okamoto. *Denki Hyoron* 25, 488 (1937).—When an alternating current of more than 250 V is passed to  $(NH_4)_2CO_3$  soln. with Fe or Ni as one electrode and with Al as the other, pale-bluish light appears at the Al electrode.  
J. C. I.

**74. On the dissociation pressures of  $Ni(NO_3)_2 \cdot 6H_2O$  and  $Co(NO_3)_2 \cdot 6H_2O$ .** K. Sano. *J. Chem. Soc. Japan*, 58, 1149-1150 (1937).—The dissociation pressures of  $Ni(NO_3)_2 \cdot 6H_2O$  and  $Co(NO_3)_2 \cdot 6H_2O$  were measured by static method using the spring manometer and the following relations were obtained:



$$\log P_{H_2O}(\text{mm}) = \frac{-2785.03}{T} + 9.977$$



$$\log P_{H_2O}(\text{mm}) = \frac{-2336.05}{T} + 8.653$$

From these results, some thermodynamical values were calcd. as follows.  $Ni(NO_3)_2 \cdot 6H_2O = Ni(NO_3)_2 \cdot 3H_2O + 3H_2O(L)$ .  $\Delta F_{298}^\circ = -3089$  cal,  $\Delta H_{298} = -18598$  cal.  $\Delta S_{298} = -52.04$  E.U.  $Co(NO_3)_2 \cdot 6H_2O = Co(NO_3)_2 \cdot 3H_2O + 3H_2O(L)$ .  $\Delta F_{298}^\circ = -3339$  cal.  $\Delta H_{298} = -20654$  cal.  $\Delta S_{298} = -58.10$  E.U.  
Author.



**75. Transportation value in the diaphragm for the treatment of electro-dialysis. I. II. III. S. Oka. *J. Soc. Chem. Ind. Japan*, 40, 815-822 (1937).**—(1) By passing current into a soln. divided by a diaphragm, the transportation values of ions are detd. by measuring the variation of concn. of the soln. on the both sides. (2) Studies are made of the influence of properties of the solns. (3) With an electrolyte on one side and two electrolytes on the other, the electrolysis was carried out, and the transportation value through the diaphragm was measured. The value thus obtained is compared with that in the case where only two kinds of ions take part.

J. C. L.

**76. On the saturation of non-volatile substances in aqueous solutions. T. Kume. *This Journal*, 12, 47-61 (1938).**

**77. On the sorption of heavy-water vapour by active charcoal. K. Arai. *Bull. Inst. Phys. Chem. Research*, 16, 749-756 (1937).**—The sorption isotherms for the system of heavy-water vapour and sugar charcoal activated by heating at 800°C for three hrs., were detd. by static method at 20°C, 30°C and 50°C over a range of press. below the satd. vapour press. The measurement were carried out with an app. of wholly Terex glass contg. Jackson's glass-spring manometer and McBain's quartz-spring balance. The result is in good agreement with McBain's typical isotherm for the system of water vapour and charcoal.

Author.

**78. Studies on the nature of the glass electrode potential. II. Effect of water on the potential of the glass electrode. H. Yoshimura. *Bull. Chem. Soc. Japan*, 12, 359-366 (1937).**—After the glass electrode was constructed, it was preserved in water and its potential was measured several times a day. The significance of preserving the glass electrode in water after its construction can be stated as follows: (i) It makes the hydrogen electrode function approach Haber's theoretical value, probably decreasing the cation effect on

the potential of the glass electrode, (ii) it decreases the asymmetry potential, equalizing the electromotive natures of the inner and the outer surfaces of the electrode membrane, and (iii) it facilitates the equilibration of the potential after the electrode is mounted in a soln. for test. Further to clarify the relationship of water to the potential of glass electrode, the effect of drying one surface of the electrode membrane was examd. Drying changed the asymmetry potential by raising the potential level of the side of the dried membrane surface, while it decreased the hydrogen electrode function on the same side. This membrane being kept submerged in water, the reverse effect was observed. These facts can be explained qualitatively, but not quantitatively by any of the current theories concerning the glass electrode, i.e. of Dole, of Gross and Halpern and of Horovitz.

Author.

**79. Studies on the nature of the glass electrode potential. III. On the cause of the asymmetry potential of the glass electrode. H. Yoshimura. *Bull. Chem. Soc. Japan*, 12, 443-452 (1937).**—The asymmetry potential and the hydrogen electrode function were measured on many sorts of glass electrodes. The conclusion is: (1) The hydrogen electrode function is, in most cases, less on the convex surface than on the concave surface of an electrode membrane, and the positive pole of the asymmetry potential is, in most cases, on the convex side. This difference between the hydrogen electrode functions of both surfaces and the magnitude of the asymmetry potential tend to decrease as the thickness of the electrode membrane diminishes. These facts suggest that the electromotive effect of the surface of a glass membrane is closely connected with the atomic constitution of the surface, and that the asymmetry potential originates in the difference of the atomic constitution between the inner and the outer surfaces of the electrode membrane. The intimate relationship between the hydrogen electrode function of a membrane surface and its potential level referring to the asymmetry potential can be explained qualitatively, but

not quantitatively by the current theories of glass electrode. (2) A glass membrane being regarded as an ensemble of many lamellae and many unit surfaces, the electromotive effects of these parts are different from one another. Therefore, the atomic constitution of the glass membrane is probably different in each part both lengthwise and breadthwise.

Author.

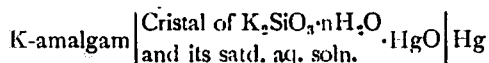
80. Studies on the dielectric constants of gases and vapours. VIII. The dipole moments of some organic compounds containing a double bond. M. Kubo. *Sci. Papers Inst. Phys. Chem. Research*, 32, 26-32 (1937).—The dielectric consts. of allyl chloride and cyclohexene were measured in the vapour state. The dipole moments were calcd. to be 1.88 D and 0.61 D resp. for the molecules of these substances. The result obtained for allyl chloride is discussed with reference to its molecular structure, and the conclusion is derived that in unsatd. hydrocarbons the part of the molecule contg. unsatd. bond is neg. end of the electric moment vector of a small but finite magnitude. Atomic polarisation of allyl chloride is 1.8 cc. That of cyclohexene is negligibly small. Author.

81. The dielectric constant of cetyl alcohol near its melting point. K. Higasi and M. Kubo. *Bull. Chem. Soc. Japan*, 12, 326-327 (1937).—Using a hetero-

dyne beat app. of 3000 kilocycles, the dielectric const. of cetyl alcohol was measured. It increases on solidification, passes through a max. at a temp. a little below the melting point and then drops to a nearly const. value at lower temps., which is of the same order of the magnitude as non-polar substances.

Authors.

82. Electrochemical study of the hydrates of potassium silicate. T. Takeda, H. Irie and E. Shibata. *J. Chem. Soc. Japan*, 58, 813-818 (1937); *J. Sci. Hiroshima Univ.*, A, 7, 327-334 (1936).—Generally speaking, K-salts have smaller number of water of crystallization than Na-salts with the same neg. ion. Under the assumption that K-silicate has a smaller number of hydrates than sodium silicate, the following cell was constructed, and its electromotive force was measured.



The results show that the curve of electromotive force-temp. between 0°C and 45°C makes only a variation at 20.9°C. A cristall prep. between 0°C~20.9°C was ascertained by analysis to be  $\text{K}_2\text{SiO}_3 \cdot 4\text{H}_2\text{O}$  and that between 20.9°C~45°C to be  $\text{K}_2\text{SiO}_3 \cdot 3\text{H}_2\text{O}$ . A different method is to be applied for analysis of cristals prep. over 45°C, because it is difficult to measure the electromotive force in that state.

J. C. L.

#### 4—COLLOID CHEMISTRY AND SURFACE CHEMISTRY

83. Thixotropy and related properties of Japanese acid-clay suspensions. B. Tamamushi and H. Suzuki. *J. Chem. Soc. Japan*, 58, 507-526 (1937).—The commercial Japanese acid-clay was examd. by crushing, centrifugation and electrodialysis. The thixotropy was most remarkable in 33% alkali salt suspensions. The value of this thixotropy and the swelling property may be arranged as follows:  $\text{Li}^+ > \text{Na}^+ > \text{K}^+ (< \text{Ca}^+)$ . The reaction of  $\text{H clay} + \text{NaOH} \rightleftharpoons \text{Na clay} + \text{H}_2\text{O}$  and that of

$\text{H clay} + \text{NaCl} \rightleftharpoons \text{Na clay} + \text{HCl}$  are considered by measuring pH of the suspensions.

J. C. L.

84. Note on a theory of the expanded film. K. Ariyama. *Bull. Chem. Soc. Japan*, 12, 335-337 (1937).—The consideration is made of the sudden appearance of micelles in the F-a curve for the equation of the following form proposed by Langmuir:  $(F - F_0)(a - a_0) = kT$ , where F is the two dimen-

sional gas press.,  $a$  the surface area for a molecule,  $T$  the absolute temp.,  $k$  the Boltzmann's const.  $F_0$  and  $a_0$  appear as consts. to be detd. by expts. Assuming that there exists the same phenomenon as the existence of the sharp critical temp. at which the anisotropy of a liquid cristal disappears, Born's equation,  $\mu^2 = (9kTc/4\pi n)$ , of the relation between the electric moment  $\mu$  of the molecule and the critical temp.  $T_c$ , was applied to the myristic acid films. Taking  $V_c$  (critical volume  $= 1/n = (4\pi/9) (\mu^2/kT)$ ), the relation between  $V_c$  and  $1/T$  was measured, and it was found that  $V_c$  should vary inversely as the temp.  $\mu$  of the myristic acid was calcd. with the above formula to be  $2.5 \times 10^{-18}$  e. s. u. This value seems to be quite reasonable and agrees with that already reported.

J. C. L.

**85. On the protecting colloids "Protalbinic" and "Lysalbinic" acids.** S. Inoue. *J. Soc. Chem. Ind. Japan*, 40, 576-577 (1937).—Almost no studies have been made on the protecting properties of these acids beyond those of R. A. Gortner (*J. Amer. Chem. Soc.*, 1917, 39, 2735; 1920, 42, 595) and R. Zsigmondy (*Kolloidchemie* 1920). The author has done some expts. with the protectors which have been prepd. by the action of solns. of different concns. (1-30%) of sodium hydroxide upon egg albumen. The surface tension and the gold number of sodium salts of these acids have been detd. Both protalbinic and lysalbinic acids which are prepd. by this method show a considerably deviated values of the surface tension and the gold number according to the concn. of sodium hydroxide used for the preparation of the acids, and it is clear that the powerful protecting "acids" are obtained only when dilute alkali soln. is added to egg albumen. Author.

**86. Sorption of acetylene and hydrogen by diatomaceous earth mixed with palladium.** I. Sano. *J. Chem. Soc. Japan*, 58, 393-409 (1937).—The present expt. was undertaken to investigate the relationship between the catalytic activity and the absorptive capacity of the palladized diatomaceous earth

catalysts used for the hydrogenation of acetylene. The catalysts were prepd. by suspending diatomaceous earth in a mixed soln. of palladium chloride and formaldehyde and adding, drop by drop, a soln. of potassium hydroxide until the soln. becomes slightly alkaline to deposit subdivided palladium on the diatomaceous earth, the compns. being 50, 100, 250, 500, 750 and 1000 grams of diatomaceous earth per one gram of palladium. These were dried by heating at 360°C. and evacuating to high vacua for several hrs. and used as sorbent for sorption of acetylene and hydrogen at 100°C. and 2/3 atmospheric pressures. In the case of acetylene, the results may be explained by assuming the entrance of acetylene molecules into the inner pores of diatomaceous earth persisting after the evaporation of water molecules, palladium particles in the catalysts functioning as supporters of the inner pores against their coalescence as well as barriers against the entrance of acetylene molecules. In the case of hydrogen, there holds a linear relation between the quantities of diatomaceous earth mixed with one gram of palladium and the amts. of hydrogen to be sorbed by one gram of palladium contd. in the catalyst, hydrogen being assumed to be sorbed by palladium particles and not by diatomaceous earth. This indicates that palladium particles dispersed in diatomaceous earth may be considered to exist in the more finely divided state as the palladium content is decreased and that hydrogen is adsorbed on the surfaces and not absorbed under the conditions described above. The applicability of the catalysts to the hydrogenation of acetylene is discussed.

Author.

**87. On the viscosity anomaly and the elasticity of concentrated aqueous solutions of sodium oleate.** F. Hirata and F. Wada. *J. Chem. Soc. Japan*, 58, 826-837 (1937).—Using the microscopic method of measuring viscosity of liquid proposed by the authors [*cf. Bull. Chem. Soc. Japan*, 10, 507 (1935)], the apparent viscosity of concd. aqueous solns. (8.30%; 13.95%; 16.60%; 27.90%) of sodium oleate, have been measured

under different temps. and presss. By the examn. of the exptl. results, it was found that the existence of viscosity anomaly has relations with the concn. of the solns., the temp. of measurements and the lapse of time after the prepn. of soln., and that in certain solns. there is a special state of the flow which indicates the existence of rigidity, although the viscosity anomaly of these solns. has already disappeared by the sufficient lapse of time. A relation between the apparent viscosity  $\eta$  and the time of measurement  $t$  has been found; in the case of certain solns. which show the absence of the elasticity, there exists a linear relation between  $\log \eta$  and  $t$ . On the other hand, in the case of certain solns. which show the existence of elasticity, it was found that there exists linear relations between  $\log \eta$  and  $t$ , separately in the two ranges of the exptl. temp. that is, the range of higher temps. at which the elasticity of the soln. does not appear and the range of lower temps. at which the existence of the elasticity can be recognized. Consequently, the relation can be shown in a succession of two linear lines which have different inclinations resp. Authors.

**88. The diffusion of electrolytes in agar gels. I. II.** S. Matuura. *J. Chem. Soc. Japan*, 58, 819-825 (1937).—I. The velocity of diffusion of an electrolyte. Diffusion velocity of the electrolytes (KCl, LiCl,  $K_2SO_4$ ) was measured in the temp. range  $10^\circ C$ – $20^\circ C$ . The diffusion consts. are independent of the concn. of the gels, and they increase with temp.

II. Diffusion of mixt. of two electrolytes. Diffusion velocities of KCl +  $K_2SO_4$  were measured.  $Cl^-$  increases its diffusion velocity in the presence of  $SO_4^{--}$ , and  $SO_4^{--}$  decreases its velocity in the presence of  $Cl^-$ . Namely, the diffusion of the faster ion is accelerated by the slower ion, while the diffusion of the

slower one is retarded by the faster one.

Author.

**89. A study of active carbon. III. Adsorbing power of active carbon in gaseous phase.** T. Katta and T. Fukuyama. *Eisei Shikensho Hokoku*, 49, 156-176 (1937).—Decolourizing and adsorbing power of active carbon were examd. with respect to the solns. of dyestuffs, petroleum oil coloured with asphalt, alkaloids, ferments, amino acids, peptones and proteins. It was found that the active carbon can be classified into two types,  $\alpha$  and  $\beta$ , just as active clay, from the observation of its decolourizing and adsorbing power. Many expts. showed that the decolourizing and adsorbing power of the  $\alpha$  type are slight for petroleum oil coloured with asphalt, pancreatin, peptone, albumin and globulin, but they are great for asparagine, glutamic acid, arginine, white of an egg, casein, dyestuff solns. and petroleum oil. As for the  $\beta$  type, the order is reversed. Adsorbing power of the  $\alpha$  type and the  $\beta$  type is very slight for amino acids. J. C. L.

**90. Influence of decomposition products of protein on the mutual precipitating reaction of colloids.** S. Yamakoshi. *Nippon Yakubutu-Gaku Zasshi*, 24, 184-191 (1937).—Pepton, glykokoll and urea protect the pptg. reaction between congo-blue and serum albumin, ovalbumin and KCl. The pptn. of ovalbumin-congo-blue in the presence of pepton is influenced in the region where the concn. of mixt. of ovalbumin and pepton is const. J. C. L.

**91. On the adsorption of hydrogen on reduced nickel.** S. Iijima. *This Journal*, 12, 1-14 (1938).