

trapolation from the adsorption data of Emmett and Brunauer. The value of q is 35,000 calories at 3.1 cc. of nitrogen adsorbed, and since $\alpha/v_m = 2900$ calories, $q_0 = 35,000 + (3.1)(2900) = 44,000$ calories. Using the experimental values of E_a , and $\gamma/v_m = 2100$ calories, one obtains by extrapolation for $E_a^0 = 10,800$ calories per mole. Thus $E_d^0 = 54,800$ calories. Substituting into (56) one gets

$$E = 54,800 - (0.276)(44,000) + (0.276)(25,000) = 49,500 \text{ cal./mole}$$

If instead of Eq. (48) we use the more correct Eq. (13) to express θ , we obtain for the apparent energy of activation of the ammonia decomposition the equation

$$E = E_d^0 - \frac{\beta}{\alpha} q_0 + \frac{\beta}{\alpha} Q - \frac{\beta}{\alpha} \left(\frac{a_0 p e^{-\alpha/RT}}{1 + a_0 p e^{-\alpha/RT}} \right) (\alpha - q_0 + Q) \quad (57)$$

In the derivation of this equation we have neglected 1 in the numerator in comparison with $a_0 p$ in Eq. (13). The first three terms on the right side of Eq. (57) are the same as in Eq. (56). The other terms in the present case amount at most only to about 500 calories. Thus the calculated value of the apparent energy of activation of the decomposition of ammonia over doubly promoted iron catalyst 931 is approximately 49,000 calories per mole. This is to be compared with the experimentally determined value of 45,600 \pm 2000 calories per mole, obtained by Love and Emmett.⁸ The agreement may be considered fair, since in the calculation of E the temperature dependence of all but the exponential terms was neglected.

In conclusion we wish to express our great indebtedness to Professor Edward Teller of George Washington University for the help and criticism he gave us in the preparation of this paper.

Summary

1. Equations were derived for the rate of adsorption, the rate of desorption and the adsorption isotherm for the cases (a) when the surface is heterogeneous, and the heat of adsorption and the energies of activation of adsorption and desorption exhibit linear variations between their maximum and minimum values, and (b) when there are forces of attraction or repulsion between the adsorbed particles, and the heat of adsorption and the energies of activation of adsorption and desorption vary linearly with the fraction of the surface covered. It was shown that these equations in the appropriate adsorption regions reduce to the equations published by Temkin and Pyzhev.

2. With the help of these equations adsorption isotherms of nitrogen on iron catalysts were calculated from rates of adsorption data. The calculated isotherms show very good agreement with the experimental isotherms.

3. Using the constants evaluated from rates of adsorption data, a kinetic equation was derived for the rate of ammonia decomposition on doubly promoted iron catalyst 931 that agrees well with the experimentally found equation. An approximately correct value for the apparent energy of activation of the decomposition was also obtained from the adsorption data.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE COLLEGE OF WASHINGTON]

Molal Volumes of Solutes. VI. Potassium Chlorate and Hydrochloric Acid

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In the fourth paper of this series² the available precise data of molal volumes of electrolytes at low concentrations have been reviewed. It was concluded that this material definitely confirms the limiting law previously derived from the theory of Debye and Hückel. However, as the experimental basis is small, new data are desirable, especially in view of some objections which

have been raised against the validity of the limiting law. Moreover, accurate data properly extrapolated will be useful in several questions: first, in a systematic classification of the individual deviations from the limiting laws occurring in the thermodynamic properties at moderate concentrations; second, in efficient tests of Born's equation as carried out for acetic acid in the fifth paper³ of this series. Finally, according to Fajans,⁴ we

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(2) O. Redlich, *J. Phys. Chem.*, **44**, 619 (1940).

(3) O. Redlich and J. Bigeleisen, *Chem. Rev.* (1942).

(4) K. Fajans, *J. Chem. Phys.*, **9**, 283 (1941).

may expect some application to the old problem of the dissociation of strong electrolytes.

Potassium chlorate is one of the six electrolytes listed by Stewart⁵ as strictly contrary to the limiting law because available data indicated a *decrease* of the molal volume with increasing concentration.

Hydrochloric acid was examined because the limiting law has been confirmed up to now only in the case of salts. Moreover, Wirth's⁶ precise results disagree with this law. In addition, data for this acid were required for testing⁸ Born's equation.

An extremely high precision was required, especially in the latter case. Presupposing that the relative deviations of the molal volume from the limiting law will be of the same order of magnitude as the deviations of the activity coefficient,⁷ we estimated that the error in the density should be not more than a few units of the seventh place.

Two sufficiently precise methods have been developed by Geffcken, Beckmann and Kruis. The first,⁸ the magnetic float method, was originated by Lamb and Lee.⁹ The second¹⁰ is a determination of the volume change on mixing, a principle used earlier by Baxter and Wallace.¹¹ Both are cumbersome. We chose Kohlrausch's hydrostatic balance method,¹² encouraged by Wirth's successful use of this device. By some changes the precision of the other two methods and at the same time a somewhat simpler and quicker procedure have been achieved.

Experimental Details.—The advantages of a difference method (one sinker in the solution, the other in water) are obvious. We believe that it is important to start each run with a "zero determination" (both sinkers in water) and to prepare the solutions *in situ* by adding weighed amounts of a stock solution or of the pure substance. Thus the influences of minor impurities of the water used and of small changes of adjustment are eliminated. In addition, time and labor are saved.

The size of the sinkers (520 cc.) was limited by the inconvenience of preparing and handling too large amounts of purified and precisely standardized solutions, and by the

minimum distance between sinker and vessel considered necessary to prevent sticking. To obtain satisfactory operation with a distance as small as 5 mm., careful alignment of the two vessels as to distance from each other and vertical mounting was required. The vessels, made of Pyrex tubing of 80 mm. i. d., were fitted snugly in two holes cut in the horizontal plate of a heavy T-shaped aluminum casting. The conical lower ends rested in aluminum cups screwed to the vertical plate of the T-casting by means of brass bolts. Covers were turned out of $\frac{3}{8}$ in. bakelite sheet. Aluminum casting, thermostat and balance were mounted on an iron angle frame. The error of alignment did not exceed 1 mm.

To ensure thorough mixing of the solution it was necessary to provide the solution vessel with a side tube through which part of the solution could be sucked from the bottom of the vessel to a sealed-on bulb.

The sinkers, blown of Pyrex tubing of 70 mm. o. d., were cigar shaped and adjusted by means of small lead shot to an average density 1.145. The suspensions were fastened to spherical buttons on top of the sinkers. The lower parts of the suspensions consisted of 0.25-mm. platinum wire, frequently plated with platinum black, the upper parts of silver wire.

The thermoregulator was made of 10-mm. glass tubing (wider containers are inefficient) and filled with carbon tetrachloride, which is more convenient than toluene. The vacuum tube relay was adjusted to a grid current of 0.6 milliamperes. A grid current like this is sufficiently low to prevent sparking of the thermoregulator contact and can be obtained with the simplest arrangement, namely, with an inexpensive tube (no. 45), a moderately-priced power relay (2000 ohms, 6 milliamperes), operation on 110 v. a. c., and the use of a filament voltage below normal as a protection against fluctuations of the main line voltage. According to our previous experiences, temperature can be kept constant within 0.001° by careful construction and adjustment of the usual device. In our case, slow fluctuations, occurring to the extent of a few thousandths of a degree during a run, were without consequence.

To prevent formation of air bubbles water was kept above 25° before use. Owing to the addition of stock solution, the length of submerged suspension varied during a run. An appropriate correction was calculated as a function of both the filling height and the density of the solution.

Water was redistilled in a Pyrex still in an atmosphere of purified air. Potassium chlorate (Mallinckrodt Analytical Reagent) was recrystallized, hydrochloric acid (same brand) redistilled. The salt was dried at about 120° to constant weight, the stock solution of the acid standardized by gravimetric determination of chloride. Solutions were made by weight (reduced to vacuum), reliable to 1:10,000. $KClO_3 = 122.553$; $HCl = 36.465$.

Results.—The results are listed in Tables I and II (*c* concentration in moles per liter, *d* density¹³ of the solution, *d*⁰ density of water, ϕ apparent molal volume in ml./mole). Several

(13) In the first four papers of this series the weight of one ml. was called specific weight or specific gravity, in accordance with German usage.

(5) G. W. Stewart, *J. Chem. Phys.*, **7**, 381, 869 (1939).

(6) H. E. Wirth, *THIS JOURNAL*, **62**, 1128 (1940).

(7) Cf. Landolt-Börnstein, "Tabellen," 3rd supplement, p. 2143.

(8) W. Geffcken, Ch. Beckmann and A. Kruis, *Z. physik. Chem.*, **B20**, 398 (1933).

(9) A. B. Lamb and R. E. Lee, *THIS JOURNAL*, **35**, 1666 (1913).

(10) W. Geffcken, A. Kruis and L. Solana, *Z. physik. Chem.*, **B35**, 317 (1937).

(11) G. P. Baxter and C. C. Wallace, *THIS JOURNAL*, **38**, 70 (1916).

(12) (a) F. Kohlrausch and W. Hallwachs, *Wied. Ann. d. Phys.*, **50**, 118 (1893); (b) F. Plato, J. Domke and H. Harting, "Wiss. Abhandlungen der Normaleichungskommission," 2 Heft, J. Springer, Berlin, 1900; (c) H. E. Wirth, *THIS JOURNAL*, **59**, 2549 (1937); (d) W. Prang, *Ann. Physik.* (5) **31**, 681 (1938).

runs, especially early ones, were disturbed by lack of adjustment and have been omitted. No single determination has been left out.

The results are represented by the equations

$$\phi = 45.677 + 1.86c^{1/2} + 0.418c \quad (\text{KClO}_3; 24.81^\circ)$$

$$\phi = 17.830 + 1.86c^{1/2} - 1.15c \quad (\text{HCl}; 25.00^\circ)$$

These empirical equations should not be extrapolated to higher concentrations than covered by our measurements.

TABLE I

MOLAL VOLUMES OF POTASSIUM CHLORATE IN AQUEOUS SOLUTION AT 24.81° (ML./MOLE)

c	$10^7 (d - d^0)/d^0$	ϕ	$10^3\delta\phi$	$10^7\delta d$
0.008710	6711	45.861	5	0
.010400	8012	.874	3	0
.012735	9805	.920	28	-4
.029083	22363	46.018	12	-3
.037754	29035	.004	-51	19
.039931	30680	.079	13	-5
.054768	42051	.132	-3	2
.064056	49165	.160	-14	9
.091097	69813	.276	0	0
.14088	107765	.417	-17	
.14572	111401	.460	12	
.17587	134315	.541	11	
.20796	158697	.600	-12	
.27062	206036	.778	19	
.36786	279384	.963	4	
.46054	349119	47.106	-26	
.56917	430180	.330	12	
.66033	498161	.471	7	

TABLE II

MOLAL VOLUMES OF HYDROCHLORIC ACID IN AQUEOUS SOLUTION AT 25.00° (ML./MOLE)

c	$10^7 (d - d^0)/d^0$	ϕ	$10^3\delta\phi$	$10^7\delta d$
0.003478	646	17.986	50	-2
.003804	710	.892	-49	2
.005889	1096	.906	-60	4
.005896	1095	18.008	42	-2
.008414	1564	17.983	-8	1
.011167	2071	18.025	11	-1
.011182	2073	.029	15	-2
.019883	3677	.077	8	-2
.020868	3855	.098	23	-5
.029099	5375	.101	-13	4
.039449	7271	.141	-12	5
.062087	11403	.206	-17	10
.080060	14650	.273	9	-7
.090978	16637	.285	-1	1
.12173	22194	.340	1	-1
.14047	25573	.367	1	-1
.17106	31081	.402	-1	2
.18895	34294	.422	0	0

A discussion of the deviations from these equations is complicated by the fact that according to

$$\delta\phi = -\frac{1000}{d^0} \frac{\delta d}{c} + \frac{1000}{d^0} \frac{d - d^0}{c} \frac{\delta c}{c}$$

there are two groups of sources of error which affect the measurements in entirely different ways. At high concentrations $\delta\phi$ is determined by the second term, which is approximately constant in the whole range. At low concentrations the first term far outweighs the second term. One has to consider, therefore, the deviations δd at low concentrations, and $\delta c/c$ or $\delta\phi$ at high concentrations.

If in the case of hydrochloric acid all deviations are attributed to the density determination, a mean square error $\delta d = \pm 4 \cdot 10^{-7}$ results. Actually the precision of the density determination is even better because the $\delta c/c$ term is not negligible at the higher concentrations. This is a very satisfactory result, as the sensitivity of the hydrostatic balance (0.1 unit of the scale) corresponds to $\delta d = 3 \times 10^{-7}$.

Taking into account the mean square value of $\delta\phi$ at the higher concentrations and the possible analytical error, we estimate the uncertainty of ϕ to be 0.02 ml./mole (potassium chlorate) and 0.01 ml./mole (hydrochloric acid).

Using data given by Joy and Wolfenden¹⁴ for 18 and 35° to correct for the small temperature difference we obtain

$$\phi = 45.711 + 1.86c^{1/2} + 0.426c \quad (\text{KClO}_3, 25.00^\circ)$$

In both cases the universal limiting slope 1.86 is fully confirmed. Some conclusions to be drawn from these results are discussed in the fifth paper³ of this series.

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Summary

The densities of aqueous solutions of potassium chlorate and hydrochloric acid have been determined with a precision of approximately 4×10^{-7} in the range of high dilution.

The limiting law of the molal volume has been confirmed. There is no reason to assume any anomaly in these substances.

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(14) W. E. Joy and J. H. Wolfenden, *Proc. Roy. Soc. (London)*, **A134**, 419 (1932).