TABLE V

LOGARITHM OF THE RELATIVE ACTIVITY COEFFICIENT OF SODIUM CHLORIDE AS CALCULATED FROM THE SOLUBILITY DATA IN TABLE III

Alcohol, w. % mole fraction	0	10	20	30	40	50
	0.0000	0.0588	0.1233	0.1941	0.2727	0.3600
HCl, m			Log of relative activity coefficient			
0.00	0.000	0.082	0.174	0.274	0.385	0.513
.10	.004	.088	.178	.275	.388	.500
.20	.008	.094	.182	.283	.395	.529
.30	.006	.098	.188	.288	.402	.532
.50	.021	.107	.194	.299	.413	.543
.75	.032	.119	.211	.312	.428	.557
1.00	.044	.132	.224	.326	.443	.573
1.50	.069	.156	.250	.356	.468	.614
2.00	.095	.185	.279	.385	.506	.652
2.50	.122	.211	.316	.421	.545	.689
3.00	.152	.245	.342	.456	.588	.732
3.50	.183	.279	.371	.497	.629	.785
4.00	.215	.313	.413	.545	.682	.838

acid–sodium chloride solutions of constant total ionic strength equal to unity has been studied from 0 to 50° using methyl alcohol–water mixtures as solvent. In accordance with earlier measurements of Åkerlöf it was found that log γ_{HCl} varies linearly with the acid concentration and the slopes of the curves are independent of the alcohol concentration at least within the range studied. The solubility of sodium chloride at 25° in methyl alcohol–water mixtures with hydrochloric acid at various concentrations has also been measured. As in the case of the pure solvent mixtures the logarithm of the activity coefficient of sodium chloride varies in the range studied linearly with the alcohol mole fraction independent of the acid concentration.

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Potentiometric Titration of Acids in Mixtures of n-Butanol and Water

BY R. N. EVANS AND J. E. DAVENPORT

The study of the strength of acids in n-butanol has been carried out both potentiometrically and colorimetrically in an attempt to correlate the thermodynamic behavior of acids in aqueous and non-aqueous solvents.[1-3] It has been demonstrated clearly that the relative strengths of acids vary in a manner which bears some relation to the dielectric constant of the solvent. Further confirmation of the fact that acids become stronger or weaker when compared to a single standard acid as the nature of the solvent is varied was observed by us in connection with our determination of acids in insulating oil. Potentiometric titration of a mixture of picric and benzoic acids each in 0.00005 M concentration gave one point of inflection in water and in equal molarity in n-butanol gave two points of inflection. It has been stated frequently that two acids must differ approximately by 10^3 in acid constants in order that two points of inflection may occur in the potentiometric titration curve. Although the effect of concentration has been implied, it is not generally emphasized that the appearance of two points of inflection is a function of concentration since many acids of the weak type are almost

completely dissociated in 0.00005 M aqueous solutions. In Table XI (reference 3) the ratio of picric acid constant to that of benzoic acid in n-butanol is 1.08 × 10^6 whereas in water the ratio is 2.5 × 10^3. It is apparent that the four-hundred fold increase in the ratio in n-butanol over that in water offsets the effect of lowered concentration.

In Fig. 1, the results of the titration of equivalent amounts of picric and benzoic acids in several water–n-butanol mixtures are shown graphically. The procedure and apparatus have been described elsewhere.[4] The cell used in all curves except the upper two was 0.1 N calomel (aqueous)/x solution/glass/x solution/0.1 N calomel (aqueous). One hundred ten milliliters of solution was prepared containing the indicated amount of acids and water and, after removal of carbon dioxide by bubbling purified nitrogen, 10 ml. was placed inside the glass bulb and 100 ml. in the titration beaker. Since 1 ml. of aqueous 0.005 M acid was used in making up the 110 ml., each acid in the titration beaker was approximately 0.000045 M. The two upper curves were produced employing the electrode system of reference 4—a change necessitated because of

(1) Wynne-Jones, Proc. Roy. Soc. (London), A140, 440 (1933).
(2) Wooten and Hammett, THIS JOURNAL, 57, 2289 (1935).
(3) Mason and Kilpatrick, ibid., 59, 572 (1937).
(4) R. N. Evans and J. E. Davenport, Ind. Eng. Chem., Anal. Ed., 8, 287 (1936).

the diffusion of water and alcohol at the liquid junction in the ground glass stopper of the 0.1 N aqueous calomel half-cell. The n-butanol purification was carried out as previously described except for the top curve solvent which received an additional treatment with benzene and subsequent fractionation. The trace of water represents the amount absorbed from the air during a short period of transfer. The neutralization of the strong acid was carried out without the formation of water by the addition of potassium stearate.

Commencing at the 100% water titration medium up to a trace of water the picric acid point of inflection is progressively more distinct. The weak acid point of inflection is least distinct in the solvent which contained the least amount of water. If an arbitrary time interval of three minutes between readings had been adopted as is expedient in routine practice, the rather obscure weak acid point of inflection would have been replaced by a flat plateau in the two upper curves. The equilibrium layers formed by shaking n-butanol and water gave results which may be more understandable with the following comments. The lower titer in the water layer was due to the greater solubility of the blank organic acid in the alcoholic phase. Theoretically the activity of water in both layers should be equal under equilibrium conditions and therefore the widely different curves for the separate phases were not expected. However, since a small amount of the other layer was maintained in the beaker during the titration, the indistinctness or total absence of the points of inflection in the alcohol equilibrium phase indicates that the neutralization reaction took place in the discontinuous (aqueous) phase. Only that portion of the reactants as demanded by their distribution coefficients would affect the electrode potential. The curve labelled 16% water approaches the equilibrium composition and in the presence of but one phase the curve is not abnormal. The secondary point of inflection in the region of the weak-acid end-point we believe is real but we are uncertain as to its cause.

Although we were primarily interested in the determination of acids, the cell was obviously designed so that the initial potential would be approximately zero. The values obtained varied between -4 to $+12$ mv. except for the experiment labelled 1% water where a pronounced

drift was observed. It was concluded that the asymmetric potential of the glass electrode, as well as the non-uniformity of the liquid junctions, would account for these variations from zero potential. There occurred also an increase in potential increment based on the theoretical results obtained in water, which was more evident as the n-butanol content of the solution was increased. A polarization effect[5] may have been responsible for the greater than theoretical increment in potential. This effect did not lower the precision with which the acids could be determined.
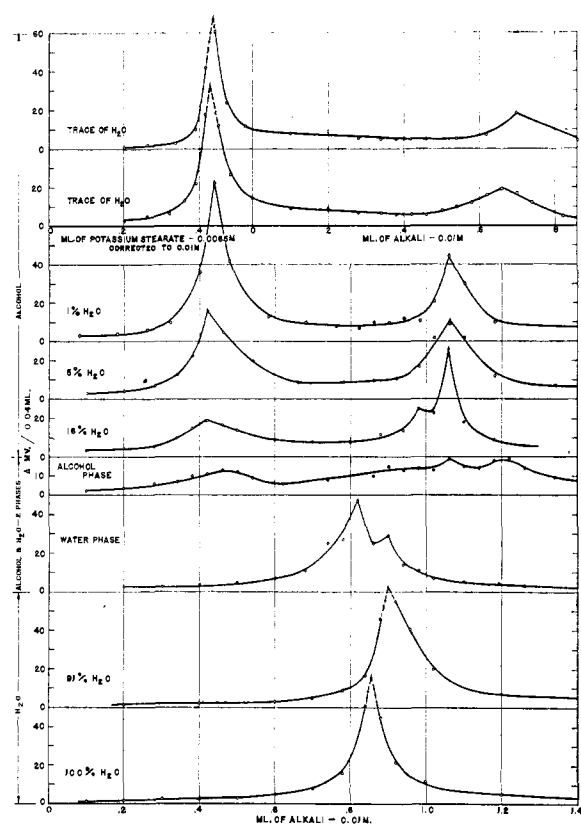

Fig. 1.—The titration of 0.000045 M picric acid and 0.000045 M benzoic acid in water–n-butanol solutions saturated with potassium picrate. Blank of 100 ml. of n-butanol equals 0.15 ml. of 0.01 M potassium hydroxide in anhydrous methanol.

The phenomenon has application in those problems in which it is desired to distinguish acids in low concentration of varied strength. Thus the catalytic combustion of sulfuretted gases in the normal atmosphere followed by absorption in water would on titration in n-butanol reveal the sulfur content of the atmosphere as distinguished

(5) R. G. Van Name and F. Fenwick, THIS JOURNAL, **47**, 9 (1925).

from carbon dioxide and other weaker acids.

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Summary

Experimental results on the potentiometric titration of acids illustrate the variation of the relative strength of acids as the character of the solvent is changed.

A Comparison of the Data of State of Normal and Para Hydrogen from the Boiling Point to 55°K.

BY EARL A. LONG[1] AND OLIVER L. I. BROWN

In the course of some low-temperature investigations on gaseous deuterium, it became of interest to us to determine a possible influence of ortho and para states on the equation of state of a gas. Although the effect of molecular rotation and the force fields set up by different spin couplings should be small, one might predict measurable differences in the PVT relationships of ortho and para forms of a gas at low temperatures. Lewis and Hanson[2] suggested the possibility of such behavior for the case of normal and para hydrogen, which should exhibit a greater difference than the two forms of deuterium. At the suggestion of Professor Gilbert N. Lewis, we have compared the two forms of hydrogen.

The apparatus and method, involving the use of a "double" constant-volume gas thermometer, have been described previously.[3]

Normal Hydrogen.—Electrolytic hydrogen from the laboratory generator was passed through a charcoal trap immersed in liquid air to remove about 0.01% oxygen impurity known to be present. The hydrogen was then passed over a white-hot platinum wire in order to restore the "normal" equilibrium between ortho and para states.

Para Hydrogen.—The para hydrogen was prepared by adsorption of hydrogen on activated charcoal at the boiling point of hydrogen for approximately five hours. A carefully purified sample of "Carbo-Norit" charcoal was used, and the apparatus was thoroughly evacuated and flushed with hydrogen before cooling to 20°K. Analysis with a Bonhoeffer thermal conductivity gage[4] showed a complete conversion at 20°K.,

corresponding to a para hydrogen content of 99.8% in the sample. The two thermometer bulbs were evacuated to 10^{-5} mm. of mercury pressure, then flushed repeatedly with normal and para hydrogen, respectively, before being filled, to ensure the absence of any traces of oxygen.

Pressure Readings.—The pressures were read in two identical glass manometers, of 16-mm. internal diameter, by comparison with a steel meter bar calibrated by the United States Bureau of Standards. The comparison instrument was a Société Génévoise cathetometer, reading to 0.02 mm. The corrections for thermal expansion of the thermometer bulbs, and the "dead-space" corrections for the small amount of gas in the connecting capillaries and fixed points of the manometers, were applied in the usual manner.[5] All pressures are expressed in international atmospheres.

In calculating temperatures, the data of Cath and Onnes[6] were used for the corrections to the normal hydrogen thermometer.

Results

Our results are expressed in terms of the empirical equation of state of Kamerlingh Onnes[7]

$$pV_A = A_A + (B_A/V_A) \qquad (1)$$

where p is given in international atmospheres, V_A (in Amagat units) is the volume expressed in terms of the normal volume as unity, and B_A is the "second virial coefficient." A_A is given by

$$A_{AT} = \left(\frac{A_{A0}}{273.10}\right) T \qquad (2)$$

(1) National Research Fellow, 1934–36.

(2) Lewis and Hanson, THIS JOURNAL, **56**, 1687 (1934).

(3) Long and Gulbransen, ibid., **58**, 203 (1936).

(4) Cf. Farkas and Farkas, "Light and Heavy Hydrogen," Cambridge University Press, 1935, pp. 20–24.

(5) Cf. Giauque and Johnston, THIS JOURNAL, **51**, 2300 (1929); Cornish and Eastman, ibid., **50**, 643 (1928).

(6) Cath and Onnes, Comm. Phys. Lab. Univ. of Leiden, No. 156, 26 (1922).

(7) Kamerlingh Onnes, ibid., No. 71 (1901).