and 45% dioxane by employing the Debye and Hückel theory as extended by Gronwall, La Mer and Sandved.

2. The results afford excellent confirmation of the general theory.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Thermodynamics of Hydrochloric Acid in Dioxane–Water Mixtures from Electromotive Force Measurements. IV. Properties of the 20% Dioxane Mixtures

BY HERBERT S. HARNED AND JOHN G. DONELSON

Harned and Morrison[1] have reported electromotive forces of the cells

$$H_2 \mid HCl\ (m),\ \text{dioxane}\ (X),\ H_2O\ (Y) \mid AgCl\text{-}Ag$$

in 20% dioxane–water mixtures and at acid concentrations varying from 0.003 to 0.1 M through a temperature range from 0 to 50°. From these results, the standard potentials of the cells have been evaluated by employing the Gronwall, La Mer and Sandved extension of the Debye and Hückel theory.[2] These measurements have now been extended to cover the concentration range from 0.003 to 3 M. From these results, the activity coefficient, relative partial molal heat content, and heat capacity of the acid have been computed and tabulated in convenient form.

Experimental Results

The experimental procedure was similar to that described in detail by Harned and Morrison.[3] The dioxane was purified by refluxing over sodium, distillation and successive freezing. The criterion of purity was the freezing point which was always within 11.77–11.78°. Assuming that the dioxane tested in this manner was pure, the composition of the dioxane–water mixtures was known to within ±0.015%. The stock solution of hydrochloric acid was standardized gravimetrically and its strength was known to within ±0.02%. The hydrochloric acid solutions used in the cells were prepared from this stock solution and their strengths were known to within the same limits.

One modification of Harned and Morrison's cell was made when working with hydrochloric acid at higher concentrations ($m > 0.2$). A piece of 2-mm. bore capillary tubing of 12–15 cm. length was sealed between the two cell compartments. This served to prevent any deposition of silver on the hydrogen electrode.

Six cells containing a given concentration of acid were measured. These were allowed to equilibrate at 25° overnight. Three of these were lowered to 0° at 5° intervals, and then finally brought back to 25°. The other three were measured at 5° intervals up to 50° and then brought back to 25°. The reproducibility of the measurements at 25° before and after these temperature changes was taken as a criterion of the accuracy of the results. Reasonable reproducibility was obtained at all acid concentrations since the readings checked to within ±0.05 mv.

The cell electromotive force was corrected to 1 atm. hydrogen pressure by the usual method making allowance for the vapor pressure of the solvent and a further correction for the lowering of the vapor pressure of the solvent by the hydrochloric acid. The latter was made by assuming Raoult's law and complete ionization of the acid. Since the largest correction due to this lowering was 0.3 mv. at 3 M acid concentration and 50°, any error caused by these assumptions is less than the experimental error in electromotive force.

The results have been expressed by the equation

$$E = E_{25} + a(t - 25) + b(t - 25)^2 \qquad (1)$$

the constants of which are given in Table I. The fifth column contains the maximum deviations in millivolts of the observed values from those

TABLE I

CONSTANTS OF EQUATION (1)

X = 20% by weight of dioxane

m	E_{25}	$-a \times 10^4$	$-b \times 10^6$	$\Delta_{(\text{max.})}$	$\Delta_{(\text{av.})}$
0.11139	0.33332	2.774	3.48	0.05	0.02
.20314	.30548	3.585	3.30	.05	.02
.25252	.29437	3.926	3.32	.05	.01
.40348	.27110	4.618	3.16	.04	.02
.7067	.24118	5.394	3.08	.06	.03
1.0341	.21897	5.920	2.80	.08	.04
1.5440	.19249	6.426	2.52	.06	.03
2.0691	.17015	6.811	2.22	.07	.03
3.0977	.13328	7.319	1.98	.06	.03

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[1] Harned and Morrison, THIS JOURNAL, **58**, 1908 (1936).

[2] Harned, *ibid.*, **60**, 336 (1938).

[3] Harned and Morrison, *Am. J. Sci.*, **33**, 162 (1937).

calculated by this equation and the last column the average deviations.

Harned and Morrison[1] obtained results at ten concentrations between 0.003 and 0.1 *M* which when combined with our observations yielded observations at nineteen suitable concentrations. All these results were smoothed to round concentrations as follows. The values of E_{25} were obtained at round concentrations from the plot of $E_{25} + 0.1183 \log m$ *versus* $\log m$. Smoothed values of a and b were also obtained graphically. Final values of these quantities which are suitable for computation of the thermodynamic properties are given in Table II.

TABLE II

SMOOTHED ELECTROMOTIVE FORCES FROM 0.003 TO 3 *M*

CONSTANTS OF EQUATION (1)

m	E_{25}	$-a \times 10^4$	$-b \times 10^6$
0.005	0.48086	−1.87	3.61
.007	.46445	−1.38	3.59
.01	.44722	−0.84	3.58
.02	.41409	0.19	3.55
.03	.39484	0.79	3.53
.05	.37074	1.54	3.51
.07	.35494	2.03	3.49
.1	.33829	2.56	3.46
.2	.30575	3.55	3.35
.3	.28606	4.14	3.26
.5	.25991	4.90	3.10
.7	.24170	5.40	2.97
1	.22099	5.95	2.78
1.5	.19453	6.58	2.52
2	.17291	7.02	2.31
3	.13689	7.67	1.99
	$E'_{0(25)}$	$-a_0$	$-b_0$
$0 (a = 1)$	.20303	7.605	3.70

In the last row of the table are given the constants of the equation for the standard potentials of the cells, namely

$$E'_0 = E'_{0(25)} + a_0(t - 25) + b_0(t - 25)^2 \qquad (2)$$

The values of $E'_{0(25)}$, a_0 and b_0 are those obtained by Harned[2] by the use of the Gronwall, La Mer and Sandved[4] extension of the Debye and Hückel theory.

Activity Coefficients

Values of the activity coefficient, γ, at some of the temperatures are given in Table III. These have been computed by employing the equation of the cell

$$\log \gamma = \frac{E - E'_0}{2k} + \log m \qquad (3)$$

where k equals $2.3026\ RT/F$.

Relative Partial Molal Heat Content

The relative partial molal heat content, $\overline{L}_2$, is related to the electromotive force of the cell and its standard potential according to the equation

$$\overline{L}_2 = FT^2 \frac{\partial}{\partial T}\left(\frac{E - E'_0}{T}\right) \qquad (4)$$

Equations (1) and (2) express E and E'_0 as functions of t. By substituting $T - 273.1$ for t in these equations, introducing the functions obtained for E and E'_0 in equation (4) and performing the integration, $\overline{L}_2$ is expressed by

$$\overline{L}_2 = \alpha + \beta T^2 \qquad (5)$$

α and β are given by

$$\alpha = -23{,}074\ [(E_{25} - E'_{0(25)}) - 298.1\ (a - a_0) + 88{,}864\ (b - b_0)] \qquad (6)$$

$$\beta = 23{,}074[b - b_0] \qquad (7)$$

respectively.[5] $\overline{L}_2$ is in calories.

TABLE III

ACTIVITY COEFFICIENTS

m	γ_0	γ_{10}	γ_{20}	γ_{25}	γ_{30}	γ_{40}	γ_{50}
0.005	0.902	0.900	0.898	0.896	0.895	0.892	0.889
.007	.889	.886	.883	.880	.880	.876	.871
.01	.872	.869	.865	.862	.861	.857	.851
.02	.835	.830	.825	.821	.820	.814	.808
.03	.811	.805	.800	.796	.795	.788	.781
.05	.780	.774	.768	.763	.762	.755	.748
.07	.759	.753	.746	.740	.740	.732	.725
.1	.736	.729	.722	.720	.716	.708	.701
.2	.696	.688	.681	.676	.673	.665	.656
.3	.682	.675	.667	.661	.658	.649	.639
.5	.684	.675	.666	.660	.656	.646	.633
.7	.649	.690	.679	.672	.667	.655	.641
1	.736	.725	.712	.704	.698	.683	.666
1.5	.830	.815	.797	.786	.777	.755	.732
2	.959	.938	.913	.898	.885	.855	.823
3	1.337	1.293	1.245	1.219	1.195	1.141	1.085

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(4) Gronwall, La Mer and Sandved, *Physik. Z.*, **29**, 358 (1928).

(5) Harned and Thomas, THIS JOURNAL, **58**, 761 (1936).

Values of α and β are given in Table IV. Since the relative partial molal heat capacity, $(\overline{C}_p - \overline{C}_{p_0})$, may be computed by the equation

$$(\overline{C}_p - \overline{C}_{p_0}) = 2\beta T \qquad (8)$$

the data in the table afford a very brief method of expressing all the heat data.

TABLE IV

PARAMETERS OF EQUATIONS (7) AND (8)

m	$(-\alpha)$	$\beta \times 10^3$	m	α	$\beta \times 10^3$
0.005	77	2.08	0.2	298	8.08
.007	77	2.54	.3	435	10.15
.01	72	2.77	.5	682	13.84
.02	77	3.46	.7	871	16.84
.03	87	3.93	1	1156	21.23
.05	87	4.38	1.5	1517	27.23
.07	96	4.85	2	1753	32.07
.1	144	5.54	3	2013	39.46

Summary

1. Electromotive forces of the cells

H_2 | HCl (m), Dioxane (20%), H_2O (80%) | AgCl–Ag

have been obtained at 5° intervals from 0 to 50°, and from 0.005 to 3 M concentrations.

2. From these and the results at lower concentrations obtained by Harned and Morrison, the activity coefficient, relative partial molal heat content and heat capacity of hydrochloric acid in this solvent have been computed over these ranges of temperature and concentration.

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[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICS, THE UNIVERSITY OF WISCONSIN]

The Joule–Thomson Effect in Mixtures of Helium and Nitrogen

BY J. R. ROEBUCK AND H. OSTERBERG

The measurements on the Joule–Thomson effect in air,[1,2] in helium,[3,4] in argon[5] and in nitrogen,[6] are here extended to four mixtures of helium and nitrogen. The work on mixtures of helium and air[3] had shown an unexpected situation which increases one's interest in the physics of these mixtures. Reference is made to the above articles for details of apparatus and methods. These measurements cover our usual pressure range of 1 to 200 atm., but the temperature range here of −100 to 250° is somewhat reduced. The experimental work was done in the fall of 1933 but the press of other work has delayed publication.

Liquefaction

In all the work with helium mixtures, whenever there was reason to believe that a liquid phase was present anywhere in the apparatus, the data simultaneously became unmanageably erratic. This occurred both when making readings near the condensing conditions of one constituent and when using the regenerative purifier.[2] This difficulty was not observed with pure air, due doubtless to the similarity of the condensing conditions of oxygen and nitrogen. We attribute the erratic readings to variation in composition of the mixture when the liquid phase consists largely of the more condensable constituent. The difficulties involved both in the experiments and in the subsequent use of the data, led us to avoid this situation. For this reason the experimental readings usually were not carried below −100°. This is distinctly unfortunate because data on gas mixtures in equilibrium with their liquid phases would be of great value for the study of the liquid–vapor relations.

Gas Supplies.—The helium was part of that supplied by the Bureau of Mines for the previous work on pure helium.[3] It was purified before use by passage over activated coconut charcoal cooled by liquid air as in the earlier work.[3]

The nitrogen was purchased from the Air Reduction Company. As in our previous work with pure nitrogen[6] it was used without further purification.

The mixture compositions are given in Table I. Since the air–helium mixture work had shown that the Joule–Thomson effect varied more rapidly

TABLE I

HELIUM–NITROGEN MIXTURES

No.	Helium, %	Nitrogen, %
0[3]	*100*	*0*
1	75.5	24.5
2	51.0	49.0
3	33.2	66.8
4	16.6	83.4
5[6]	*0*	*100*

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[1] Roebuck, *Proc. Am. Acad. Arts. Sci.*, **60**, 537 (1925).

[2] *Idem.*, **64**, 287 (1930).

[3] Roebuck and Osterberg, *Phys. Rev.*, **43**, 60 (1933).

[4] *Idem.*, **45**, 332 (1934).

[5] *Idem.*, **46**, 785 (1934).

[6] *Idem.*, **48**, 450 (1935).