TABLE XIII

THERMODYNAMIC FUNCTIONS OF FORMATION FOR $Pb(CH_3)_4$(g) AND $Sn(CH_3)_4$(g)

T, °K.	$(\Delta H^0)_f$, kcal./mole	$(\Delta F^0)_f$, kcal./mole	$(\Delta S^0)_f$/mole
	$Pb(CH_3)_4$(g)		
300	3.2 ± 3	35.6 ± 3.6	−108 ± 2
400	1.2	46.0	−112
500	−0.5	57.0	−115
600	−1.9	68.1	−117
	$Sn(CH_3)_4$(g)[a]		
300	−13.6 ± 10	19.0 ± 10	−109
400	−15.7	30.2	−115
500	−17.5	41.9	−119

[a] Based on $(\Delta H^0)_f$ for SnO_2 = −138.8 kcal./mole.

energy and entropy of formation of SnO_2 given by N.B.S.,[18] the heat of formation, (ΔH^0), at 300°K. was calculated. Using this, the calculated thermodynamic functions for Sn(s) and $Sn(CH_3)_4$(g), and the functions for C(graphite) and H_2(g) given in N.B.S. tables, a value of E_0^0 of −5.5 ± 10 kcal./mole, was obtained. The thermodynamic functions for Sn(s) were obtained from data given by Kelley[19] and Klinkhardt[13] and are tabulated in Table XII. From E_0^0 the functions $(\Delta H^0)_f$, $(\Delta F^0)_f$ and $(\Delta S^0)_f$ were calculated by standard methods and are tabulated in Table XIII from 300 to 500°K.

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[18] N.B.S. Circular 500 "Selected Values of Chemical Thermodynamic Properties."

[19] K. K. Kelley, Bureau of Mines Bulletin 350, (1932).

MANHATTAN, KANSAS
STORRS, CONN.

[FROM THE UNIVERSITY OF CALIFORNIA, DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, AND THE RADIATION LABORATORY, BERKELEY]

Absolute Entropies in Liquid Ammonia

BY WENDELL M. LATIMER AND WILLIAM L. JOLLY

RECEIVED MAY 15, 1953

It is shown that a simple relationship exists between the partial molal entropies of ions in water and liquid ammonia if the absolute entropy of H^+ is taken as −2 e.u. in water and −25 e.u. in ammonia. A new tabulation of thermodynamic data for ions in liquid ammonia is given.

From studies of relative ionic entropies in methanol,[1] and ammonia[2,3] and from the entropies of ionization of methanol, ethanol, acetic acid and ammonia,[4] it has been concluded that the absolute ionic entropies in these solvents are considerably more negative than the corresponding absolute entropies in water. The arguments for this conclusion are: (1) The entropies of solution of electrolytes in water are generally more positive than in the non-aqueous solvents, and (2) the entropy of ionization of water is more positive than the corresponding entropies of ionization of the non-aqueous solvents.

In the case of water, the absolute entropy of the hydrogen ion has been determined as −2.1 e.u.[5] (very close to the usual arbitrary value of 0 e.u.) and monatomic ion entropies may be well represented by the equation of Powell and Latimer[6]

$$S^0 = 3/2R \ln M + 37 - 270Z/r_e2$$

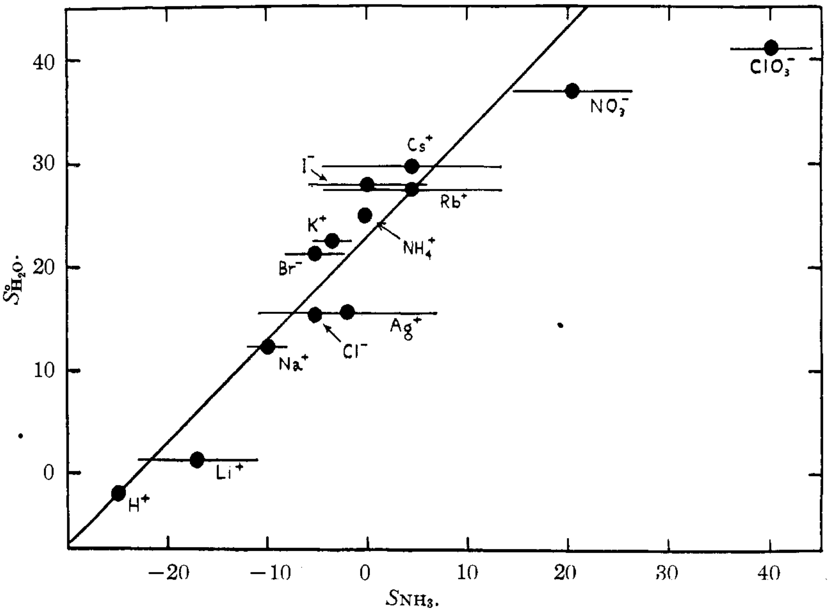

Fig. 1.

If one plots absolute partial molal entropies in water against partial molal entropies in ammonia,

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[1] W. M. Latimer and C. M. Slansky, THIS JOURNAL, **62**, 2019 (1940).

[2] W. L. Jolly, *Chem. Revs.*, **50**, 351 (1952).

[3] S. P. Wolsky, E. J. Zdanuk and L. V. Coulter, THIS JOURNAL, **74**, 6196 (1952).

[4] W. L. Jolly, *ibid.*, **74**, 6199 (1952).

[5] J. C. Goodrich, F. M. Goyan, E. E. Morse, R. G. Preston and M. B. Young, *ibid.*, **72**, 4411 (1950).

[6] R. E. Powell and W. M. Latimer, *J. Chem. Phys.*, **19**, 1139 (1951).

TABLE I

THERMODYNAMIC FUNCTIONS AT 298°K.

	ΔH_f°, kcal./mole	ΔF_f°, kcal./mole	S°, e.u.		ΔH_f°, kcal./mole	ΔF_f°, kcal./mole	S°, e.u.
H^+	0	0	0	SCN^-	−11.8		
H_2O	−71.6			Pb^{++}	21.0	13	11
F^-		−80.8		Pb_9^{----}	64		
Cl^-	−65.7	−44.1	−30.3	Tl^+		5.7	
ClO_3^-	−47.7	−17.7	15	Zn^{++}		−25	
Br^-	−59.0	−39.9	−30.3	Hg^{++}	45.2	31	35
I^-	−45.3	−29	−25	Ag^+	26	17.5	23
IO_3^-		−42.4		Mn^{++}		−26	
$Se_2^=$	−19.0			BH_4^-	−15.7		
$Te_2^=$	−27.8			Ca^{++}	−100.0	−100	−21
$Te_4^=$	−29.7			Li^{++}	−49	−54	8
NO_3^-	−77.6	−42.8	− 5	Na^+	−38.1	−43.6	15.1
NH_3	−16.1	−2.7	24.7	K^+	−40.5	−47.0	21.4
NH_4^+	−16.1	− 2.7	24.7	Rb^+	−39	−47.5	29
NH_2^-	10.1	34	−10	Cs^+	−40.5	−48	29
NH_2OH	−24.6			$^1/_2e_2^=$ (am)	40.5	44.4	2
Guanidinium ion	−20.0			e^- (am)	43.5		

both the positive and negative ions fall upon a line if the absolute entropy of H^+ in ammonia is taken as −25 e.u. This plot is shown in Fig. 1. Since the slope of the line (as drawn) is unity, the coefficient of the Z/r_e^2 term in the Powell–Latimer equation must be approximately the same for both ammonia and water. At least for monatomic ions, it would appear that absolute entropies in water are simply 23 units higher than in ammonia.

Values for NO_3^- and ClO_3^- are included in Fig. 1, but since the Powell–Latimer equation applies only to the monatomic ions, it is not surprising that they fall off the curve. The experimental data for dipositive ions in ammonia are so incomplete that it is not possible to ascertain the dependence of the entropies on the charge on the ion with any accuracy and the tentative values for Ca^{++}, Pb^{++} and Hg^{++} have not been plotted in Fig. 1.

A recalculation has been made of many of the thermodynamic functions for ions in ammonia.[7] A number of these new values differ from those previously tabulated by Jolly,[2] and a new summary is therefore given in Table I.

[7] For the detailed calculations see W. L. Jolly, University of California Radiation Laboratory Report No. UCRL-2201, May, 1953.

BERKELEY, CALIF.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Verification of a Theory of Irreversible Polarographic Waves

BY PEKKA KIVALO, K. B. OLDHAM AND H. A. LAITINEN

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Two independent schools have recently derived equations of totally irreversible waves; the equations are identical. The equation predicts that at the foot of the wave, the current obeys relationships that are typical of kinetic control; at the head of the wave, however, diffusion controlled relationships apply. Several expressions have been derived from the basic equation. Experimental verification of these expressions furnishes a convincing proof of the validity of the theory of irreversible waves.

During recent years, two independent approaches have been made to the problem of the interpretation of completely irreversible polarographic waves. The treatment employed by Delahay and Strassner[1–3] differs only in minor respects from that due to Evans, Hush and Oldham.[4–6] The basic equation of the polarographic wave, as derived by Delahay,[1,2] is identical in all but mathematical terminology from that obtained by Hush and Oldham.[6] The symbolism and method of the latter workers has been retained in the present paper because it is more amenable to mathematical treatment than the graphical procedure of Delahay.

The purpose of the theoretical section of the present paper is to present some of the implications of the theory and, in particular, to derive relationships that may be readily tested experimentally. The experimental section is devoted to the verification of these relationships. Such verifications of the theory as have hitherto been reported,[2,6] have been of a somewhat scanty nature.

Implications of the Equation of the Irreversible Wave.—The basic equation derived by Hush and Oldham[6] to express the instantaneous current, i_t (in microamperes), passed by a dropping mercury electrode in consequence of the totally irreversible reduction

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[1] P. Delahay, THIS JOURNAL, **73**, 4944 (1951).

[2] P. Delahay and J. E. Strassner, *ibid.*, **73**, 5219 (1951).

[3] P. Delahay, ONR report No. 7, Project NR-051-258 (1952).

[4] M. G. Evans and N. S. Hush, *J. chim. phys.*, **49**, C159 (1952).

[5] N. S. Hush and K. B. Oldham, *Nature*, in press.

[6] N. S. Hush and K. B. Oldham, *Trans. Faraday Soc.*, in press.