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A Polarographic Investigation of the Pseudo Acid Properties of Nitroparaffins[1]

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The nitroparaffins have long been recognized as pseudo acids. They dissolve in alkaline solution through the formation of salts according to the equation

$$\mathrm{R{-}CH_2NO_2 + OH^- \longrightarrow R{-}CH{-}NO_2^- + H_2O}$$

This neutralization is a relatively slow process and the rates of neutralization by different bases have been investigated by Maron and La Mer[3] and more recently by Pearson.[4] In both investigations the reaction rate was followed conductometrically.

De Vries and Ivett[5] reported that the wave heights for the reduction of nitroparaffins were proportional to the concentration of the nitroparaffin when 0.05 molar sulfuric acid was used as the supporting electrolyte but that this relationship was not linear when 0.05 molar sodium sulfate was used in place of sulfuric acid. When sodium sulfate was used as the supporting electrolyte the *p*H increased as the reduction progressed because hydrogen ions were used up in the reduction process. This increase in *p*H caused a shift in the equilibrium between the normal and aci-forms of the nitroparaffin in favor of the aci-form which was not reducible at the dropping mercury cathode. As the concentration of the nitroparaffin was increased the *p*H became still greater resulting in still more of the aci-nitroparaffin being formed and consequently the wave height was not proportional to concentration. The nitroparaffins could not be reduced in 0.1 *N* sodium hydroxide or 0.1 *N* tetramethylammonium hydroxide. This investigation would indicate that the polarograph would make possible the determination of the normal nitroparaffin—which is the form present in acid solution—in the presence of the aci-form and that the rate of this transformation could be determined in a buffered solution where the hydroxyl ion concentration is maintained at a constant value.

Experimental Part

Each of the nitroparaffins was purified in an all-glass Widmer fractionating column 18 inches in length. A fraction was collected having a boiling range of less than 0.5° which included the boiling point of the nitroparaffin. Stock solutions were prepared in water having a concentration of nitroparaffin of 0.002 mole per liter.

Double strength stock solutions of Sörensen glycine–sodium chloride–sodium hydroxide and McIlvaine disodium phosphate–citric acid buffers were prepared following the directions given by Clark.[6] A sufficient amount of sodium chloride was added to the citric acid solution to make it 0.2 molar with respect to sodium ion. The McIlvaine buffers were used in the *p*H range 2 to 7 and the Sörensen buffers in the *p*H range 8 to 13. A Beckman *p*H meter was used to determine the *p*H of the solutions resulting from the mixing of the appropriate buffer with an equal volume of the nitroparaffin solution.

A Sargent Model XX Polarograph was used for all measurements. The capillary used as the dropping mercury cathode had a value for $m^{2/3}t^{1/6}$ of 2.41 $\mathrm{mg.}^{2/3}\ \mathrm{sec}^{-1/2}$. The cell was H-shaped with one arm containing a saturated calomel reference electrode. The temperature was maintained at 25 ± 0.1° by means of a constant temperature bath.

Removal of oxygen was accomplished by passing nitrogen through 10 ml. of a solution of the nitroparaffin in water (0.002 molar) and through an equal volume of the desired double strength buffer. The two solutions were then introduced simultaneously into the electrolysis cell and the degassing continued for about one minute to insure adequate mixing. Five drops of a methanol solution of 0.5% brom cresol green and 0.5% methyl red were added to the buffer solution before each run as a maximum suppressor.

Timing was begun at the moment of the mixing of the

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[1] Presented before the Division of Physical and Inorganic Chemistry, Chicago, April, 1948.

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[3] S. H. Maron and V. K. La Mer, *Annals of the New York Academy of Sciences*, May, 1940, Vol. 39, page 355, and THIS JOURNAL, **60**, 2588 (1938).

[4] R. G. Pearson, *ibid.*, **70**, 204 (1948).

[5] T. De Vries and R. W. Ivett, *Ind. Eng. Chem., Anal. Ed.*, **13**, 339 (1941).

[6] W. M. Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, Maryland, 1928.

nitroparaffin and buffer solutions. A polarogram was recorded immediately after degassing and subsequent determinations of the diffusion current were made at frequent time intervals.

Discussion of Results

At a *p*H of 2.1 the diffusion current representing the concentration of the nitroparaffin did not decrease with time and it was therefore assumed that the wave height found under these conditions represented the initial concentration of each nitroparaffin at each *p*H investigated. With all four nitroparaffins studied there was a slight decrease in the concentration of the nitro-form with time, even at a *p*H as low as 5.

The effect of *p*H on the conversion of nitromethane into aci-nitromethane is shown in Fig. 1.

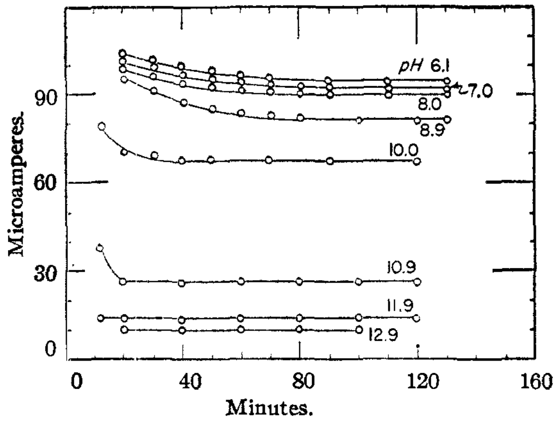

Fig. 1.—Change of diffusion current with time for nitromethane (0.001 molar): i_d at *p*H 2.1 = 23.2 microamperes; $m^{2/3}t^{1/6}$ = 2.41 mg.$^{2/3}$ sec.$^{-1/2}$.

In a solution of given *p*H there is an initial decrease in concentration of the nitromethane with time. After this initial decrease in the concentration there is no further change in the diffusion current indicating that an equilibrium is established between the nitro- and aci-forms of the compound. Equilibrium conditions were slowly established at *p*H values lower than 9. The time required under these conditions was as much as ninety minutes. However, as at a *p*H of 10 and greater the equilibrium was reached in less than ten minutes, it was impossible to obtain reliable data in this *p*H range for the calculation of satisfactory rate constants. The position of the equilibria did not vary with *p*H very much in the range 5 to 8 but became more sensitive to a change of *p*H in more alkaline solutions.

The half-wave potentials for the reduction of nitromethane became more negative with increasing *p*H up to a *p*H of about 8 and in more alkaline solutions became approximately constant at a value of about −0.95 volt. The greatest change of half-wave potential with *p*H occurred over the range of 4 to 8.

The rate of transformation of nitroethane into aci-nitroethane as a function of *p*H is shown in Fig. 2. The isomerization of nitroethane followed the same general pattern as was observed with nitromethane with two significant differences.

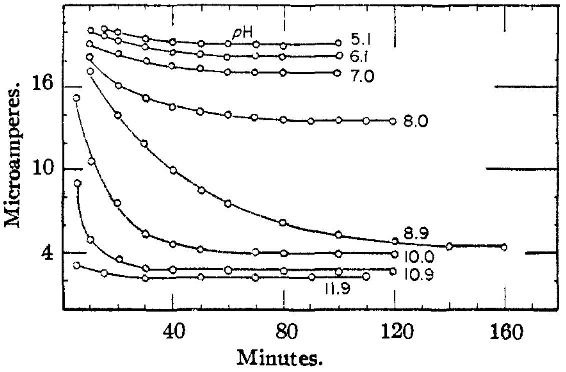

Fig. 2.—Change of diffusion current with time for nitroethane (0.001 molar): i_d at *p*H 2.1 = 21.4 microamperes; $m^{2/3}t^{1/6}$ = 2.41 mg.$^{2/3}$ sec.$^{-1/2}$.

(1) The equilibria between the nitro and aci-forms were established at about the same rate as was observed for nitromethane in the *p*H range 5 to 7 but in the *p*H range 8 to 10 it required eighty to one hundred and sixty minutes for the equilibrium to be established for nitroethane compared with ten minutes or less in the case of nitromethane.

(2) The positions of the equilibria were far more dependent upon the *p*H in the range 7 to 9 in the case of nitroethane while the nitromethane equilibria were most dependent upon *p*H in the range 9 to 12.

At a *p*H of 2.1 the wave heights for nitroethane were found to be proportional to the concentration of the nitroparaffin. Solutions buffered at a *p*H of 10.0, in which the concentration of nitroethane was made 1.0, 1.5 and 2.0 millimolar, respectively, were prepared and polarograms obtained after standing for two hours to permit equilibrium to become established. The wave height representing the concentration of nitroethane remaining in the normal nitro-form was again found to be proportional to the concentration of the original nitroparaffin. The ratio of normal nitroethane remaining at equilibrium to the original nitroethane was 0.18, 0.18 and 0.175, respectively.

The concentration of the nitroparaffin remaining in the equilibrium mixture at high *p*H values seems rather large, yet the polarographic evidence seems to indicate a true equilibrium. That the small wave might represent some other electrode process is quite unlikely in that less than one electron per molecule would be indicated by the Ilkovic equation. The wave height decreases to zero in more alkaline solution as pointed out by De Vries and Ivett.

As with nitromethane the half-wave potential became more negative with increasing *p*H and approached a constant value of about −0.95 volt in solutions of *p*H 10 or greater.

The isomerization of the nitropropanes was comparable with that observed for nitroethane except that the equilibria were established more slowly (see Figs. 3 and 4). The effect of *p*H upon the half-wave potentials was the same as that observed with nitromethane and nitroethane.

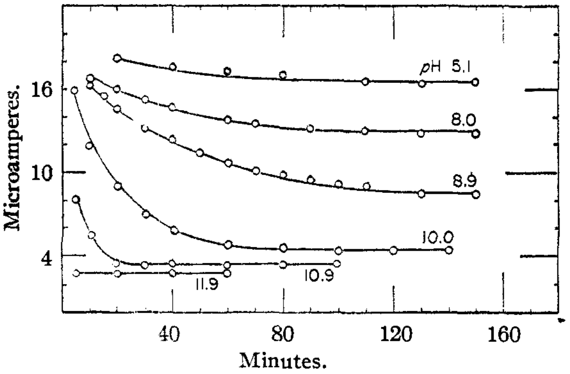

Fig. 3.—Change of diffusion current with time for 1-nitropropane (0.001 molar): i_d at *p*H 2.1 = 18.8 microamperes; $m^{2/3}t^{1/6}$ = 2.41 mg.$^{2/3}$ sec.$^{-1/2}$.

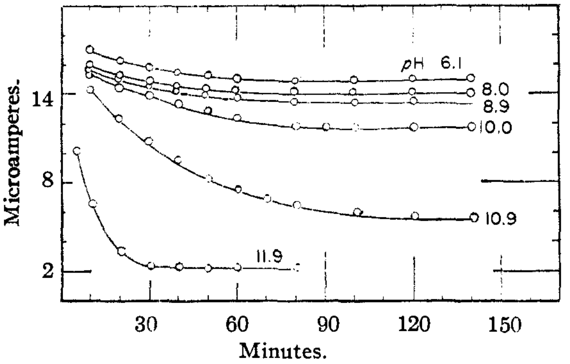

Fig. 4.—Change of diffusion current with time for 2-nitropropane (0.001 molar): i_d at *p*H 2.1 = 17.3 microamperes; $m^{2/3}t^{1/6}$ = 2.41 mg.$^{2/3}$ sec.$^{-1/2}$.

The effect of the *p*H of the solution on the concentration of the nitro form of each nitroparaffin remaining in the equilibrium mixture is shown in Table I and Fig. 5. It is of interest to note that the effect of *p*H on the position of the equilibria is about the same with nitromethane and with 2-nitropropane. However, with these two the position of the equilibria differ greatly from the equilibria obtained in the cases of nitroethane and 1-nitropropane. In the case of the first two compounds a *p*H of 9 or better is required before an appreciable amount of the nitroparaffin is transformed into the aci-nitroparaffin while the latter two produce the same effect at least two *p*H units lower.

TABLE I

THE FRACTION OF THE NITROPARAFFIN REMAINING IN THE NITRO-FORM IN THE EQUILIBRIUM MIXTURE

	*p*H of solution					
	6.1	7.0	8.0	8.9	10.0	10.9
Nitromethane	0.83	0.81	0.77	0.71	0.57	0.22
Nitroethane	.88	.79	.63	.20	.18	.13
1-Nitropropane	.85	..	.66	.42	.23	.18
2-Nitropropane	.87	.83	.82	.78	.67	.33

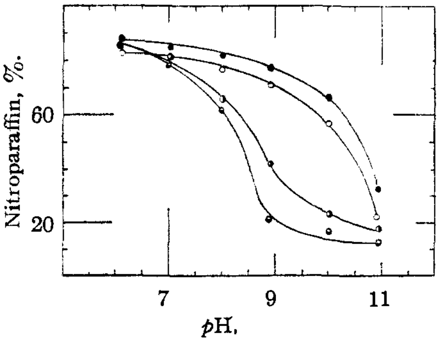

Fig. 5.—The percentage of nitroparaffin remaining in the equilibrium mixture: O, nitromethane; ⊖, nitroethane; ◐, 1-nitropropane; ●, 2-nitropropane.

Each reaction was found to be pseudo first order involving a simultaneous reverse reaction. Since the polarograph can only determine the normal nitroparaffin and cannot differentiate between the un-ionized and ionized aci-compounds, it is necessary to write a simplified equation

$$\mathrm{N} \underset{K'}{\overset{k}{\rightleftarrows}} \mathrm{A}$$

where N represents the normal nitroparaffin and A the aci-nitroparaffin which may involve both the ionized and un-ionized forms of the molecule.

The net rate of reaction can then be written

$$\mathrm{d}x/\mathrm{d}t = k(a - x) - k'x$$

where a represents the original concentration of nitroparaffin and x the amount of nitroparaffin transformed at time t. At equilibrium $k(a - x_e) = k'x_e$ where x_e is the amount of the nitroparaffin transformed at equilibrium. Substituting for k' it follows that

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{ka}{x_e}(x_e - x)$$

and the rate constant for the forward reaction may be written

$$k = \frac{x_e}{at}\ln\left(\frac{x_e}{x_e - x}\right)$$

Excellent rate constants were obtained for each nitroparaffin when this equation was used. The validity of these constants is shown in Table II and the values for all constants are given in Table III.

It is possible to use the data of Turnbull and Maron[7] to calculate the ratio of nitroparaffin to un-ionized aci-nitroparaffin at any *p*H. The polarographic data are not in complete agreement with the previous data in that too much aci-nitroparaffin is indicated at low *p*H and too little aci-nitroparaffin at high *p*H. The data also indicated that 2-nitropropane is least converted to the aci-

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[7] D. Turnbull and S. H. Maron, THIS JOURNAL, **65**, 212 (1943).

TABLE II

RATE CONSTANTS FOR THE TRANSFORMATION OF NITROPARAFFINS INTO ACI-NITROPARAFFINS

*p*H	*t*, min.	x(μa)	a(μa)	x_e(μa)	k
			Nitromethane		
6.1	20	2.7	23.2	4.2	0.0085
	30	3.1	23.2	4.2	.0073
	40	3.5	23.2	4.2	.0071
	50	3.8	23.2	4.2	.0072
	60	4.0	23.2	4.2	.0072
8.9	15	4.2	23.2	6.8	.0188
	20	4.8	23.2	6.8	.0178
	25	5.3	23.2	6.8	.0178
	30	5.6	23.2	6.8	.0174
	40	6.1	23.2	6.8	.0167
	60	6.6	23.2	6.8	.0173
			Nitroethane		
6.1	10	1.2	21.4	3.2	.0070
	20	1.9	21.4	3.2	.0068
	30	2.4	21.4	3.2	.0069
	40	2.7	21.4	3.2	.0070
	50	2.9	21.4	3.2	.0071
8.9	10	4.2	21.4	17.2	.0224
	20	7.3	21.4	17.2	.0223
	30	9.4	21.4	17.2	.0212
	40	11.4	21.4	17.2	.0221
	50	12.9	21.4	17.2	.0223
			1-Nitropropane		
8.0	20	2.8	18.8	6.1	.0094
	30	3.5	18.8	6.1	.0093
	40	4.1	18.8	6.1	.0094
	50	4.6	18.8	6.1	.0096
	60	5.0	18.8	6.1	.0093
8.9	10	2.4	18.8	10.4	.0144
	20	4.2	18.8	10.4	.0142
	30	5.6	18.8	10.4	.0142
	40	6.5	18.8	10.4	.0135
	60	8.1	18.8	10.4	.0139
			2-Nitropropane		
10.0	20	2.4	17.3	5.7	.0093
	30	3.2	17.3	5.7	.0089
	40	3.8	17.3	5.7	.0095
	50	4.3	17.3	5.7	.0095
10.9	10	2.9	17.3	11.5	.0189
	20	4.8	17.3	11.5	.0179
	30	6.4	17.3	11.5	.0186
	40	7.7	17.3	11.5	.0186
	50	9.0	17.3	11.5	.0201

TABLE III

REACTION RATE CONSTANTS FOR THE TRANSFORMATION OF NITROPARAFFINS INTO ACI-NITROPARAFFINS

(k = min.$^{-1}$)

	*p*H of the solution					
	6.1	7.0	8.0	8.9	10.0	10.9
Nitromethane	0.0072	0.0099	0.015	0.018	...	...
Nitroethane	.0070	.0092	.018	.022	0.068	0.190
1-Nitropropane	....	....	.0094	.014	.044	...
2-Nitropropane	....	....	.0078	.0081	.009	.019

form whereas it would be expected to be the most. Two factors make the two investigations not exactly comparable. Turnbull and Maron indicate that the following equilibria are involved

$$RCH_2NO_2 \rightleftarrows R\overset{-}{C}H{-}NO_2 \rightleftarrows RCH{=}NO_2^- \rightleftarrows RCH{=}NO_2H$$

The only molecular species which can be determined polarographically is the normal nitroparaffin and the latter three molecules are collectively called "aci-nitroparaffin" in this investigation. The same ratio is not being measured in the two cases.

The total ionic strength was very high in this investigation compared with the previous work and this would result in an appreciable correction for the activities of the components in the equilibrium mixture. The peculiar behavior of 2-nitropropane cannot be satisfactorily explained.

Although the rate of reaction increases with *p*H there was no direct relationship between the rate of reaction and the hydroxyl ion concentration of the solution. This might arise from the fact that hydroxyl ion is not the only base present in the solution and that the bases used as buffers may play an important role in controlling the rate of reaction. Pearson[4] observed that there was no linearity between the rates of neutralization of the nitroparaffin with amines and the base strength of these amines. Dimethylamine and trimethylamine reacted more rapidly than their basicities would warrant.

The rates of the reactions in the *p*H range 6 to 9 were found to decrease in the order $EtNO_2 \geqq MeNO_2 > n\text{-}PrNO_2 > i\text{-}PrNO_2$. The reaction rates for nitromethane and nitroethane were about the same although the isomerization of nitroethane did have a slightly higher rate at a *p*H of 8.0 and 8.9. This may not be significant because, as the *p*H was increased, the nitromethane equilibria were established so rapidly that no reliable data could be obtained for the calculation of satisfactory rate constants. There was a marked difference in the rate constants between nitroethane and the nitropropanes and at high *p*H values the rate for nitromethane was very much faster than for any of the other compounds.

An estimation of the number of electrons involved in the reduction process indicates that the nitroparaffins are probably reduced to the corresponding hydroxylamines at the dropping mercury cathode. This is in agreement with the suggestion of DeVries and Ivett[5] and is supported by the observation reported by Hass and Riley[8] that the reduction of the nitroparaffins at low temperatures results in the formation of the corresponding alkyl hydroxylamines.

The effect of *p*H upon the half-wave potentials for each of the four nitroparaffins tabulated in Table IV indicates that the half-wave potentials are all within 0.15 volt of the same value over the entire *p*H range investigated. These potentials changed with *p*H most rapidly between the values

[8] H. B. Hass and Elizabeth Riley, *Chem. Rev.*, **32**, 379 (1943).

4 and 8. With all four compounds the half-wave potentials became approximately constant at a value of about −0.95 volt (*vs.* S.C.E.) over the *p*H range 9 to 12. The half-wave potentials lie so close together that it is impossible to determine one compound in the presence of the others.

TABLE IV

THE EFFECT OF *p*H ON THE HALF-WAVE POTENTIAL

	Half-wave potentials (volts *vs.* S. C. E.)			
*p*H	Nitromethane	Nitroethane	1-Nitropropane	2-Nitropropane
2.1	−0.60	−0.63	−0.56	−0.49
4.0	.67	.71	.65	.58
5.1	.81	.82	.76	.77
6.1	.86	.86	.82	.84
7.0	.88	.90	.86	.90
8.0	.91	.93	.89	.94
8.9	.92	.94	.93	.96
10.0	.93	.95	.94	.97
10.9	.94	.95	.95	.98
11.9	.96	.95	.96	.98

The reduction probably proceeds in acid solution according to the equation

$$R—NO_2 + 4H^+ + 4e^- \longrightarrow R—NHOH + H_2O$$

while in alkaline solution the equation for the reduction probably is

$$R—NO_2 + 3H_2O + 4e^- \longrightarrow R—NHOH + 4OH^-$$

The latter equation would account for the slight effect of the *p*H of the solution upon half-wave potential in the alkaline range since the irreversible reduction is not dependent upon the hydrogen ion concentration.

Summary

The rate of transformation in buffered solutions of four nitroparaffins into the corresponding aci-nitroparaffins has been followed polarographically. The rate constants for these reactions were determined and the reactions were found to be first order involving a simultaneous reverse reaction. The positions of the equilibria were found for each compound over the *p*H range 6 to 11. The rate of reaction decreased in the following order: nitromethane > nitroethane > 1-nitropropane > 2-nitropropane.

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[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY OF MICHIGAN STATE COLLEGE]

Reactions Involving Like-Charged Ions. I. A Neutral Intermediate in Alkaline Permanganate Oxidations

BY FREDERICK R. DUKE[1]

The lattice energies of ionic crystals amount to one hundred or more kcal. per mole.[1a] When such a crystal dissolves in the form of unassociated ions the hydration energy is approximately the magnitude of the lattice energy. The energy of dissociation of hydrated oppositely charged ions is small.[2] We may, therefore, conclude that like-charged ions can readily collide on the periphery of their solvation spheres and that appreciably closer approach of the ions in solution is prohibited. The problem of the activation energy of reaction through the solvation layers is difficult to treat theoretically, but published experimental evidence, some of which is cited below, indicates that the energy requirements are often large.

In the general case of acid–base reaction involving like-charged ions, typified by $[Fe(OH)_2(H_2O)_4]^+ + H^+ \rightleftarrows [Fe(OH)(H_2O)_5]^{++}$, the obvious low energy path is provided by direct reaction of a neutral base[3] (followed, in some cases, by dissociation of ions)

$$[Fe(OH)_2(H_2O)_4]^+ + H_2O \rightleftarrows [Fe(OH)(H_2O)_5]^{++} + OH^-$$

Oxidation–reduction reactions of this type occasionally are clearly oppositely charged ionic reactions, such as the reaction of Fe^3 with Sn^2 in hydrochloric acid solution, where negative chloride complexes of iron have been shown to provide the reaction path.[4] Certain other electron-transfer reactions between like-charged ions proceed very slowly; for example, Sn^2 and Fe^3 react 10^{-5} to 10^{-6} as fast in perchloric as in hydrochloric acid.[3] Even in this case, a minute concentration of complex involving perchlorate as well as hydroxyl *may* provide the reaction path. $[Co(NH_3)_6]^{+3}$ does not exchange with Co^{++}.[5] Other examples might be cited to show that the energy involved in electron transfer through solvation spheres is high.[6]

It is interesting to calculate the magnitude of concentration of neutral or oppositely charged intermediate necessary to provide the reaction path, taking reasonable numbers for the equation $k = Ke^{-\Delta H/RT}$, where k is the specific rate constant, K a constant involving the frequency factor and the entropy of activation, and ΔH the experimental energy of activation. If the entropies for the processes involving like-charged ions on the one hand and a neutral or oppositely charged intermediate on the other, may be considered ap-

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[1a] Helmholz and Mayer, *J. Chem. Phys.*, **2**, 245 (1934).

[2] Fuoss and Kraus, THIS JOURNAL, **55**, 1019 (1933).

[3] Gorin, *ibid.*, **58**, 1794 (1936).

[4] Robertson and Law, *Trans. Faraday Soc.*, **31**, 899 (1935).

[5] McCallum and Hoshowsky, *J. Chem. Phys.*, **16**, 254 (1948).

[6] Harbottle and Dodson, THIS JOURNAL, **70**, 880 (1948); Prestwood and Wahl, *ibid.*, **70**, 880 (1948); Van Alten and Rice, *ibid.*, **70**, 883 (1948).