The fact that the decomposition over 931 does not show a BC region but behaves as though it is in the AB region is consistent with the fact that 931 chemisorbs more nitrogen per unit iron surface at a given temperature and partial pressure of nitrogen than does 954 and with the inability of 931 to permit —NH or —NH_2 to be adsorbed on its surface.

Catalyst 973, as indicated in Figs. 11 and 12, appears to resemble catalyst 954 as far as the dependence of rate of ammonia decomposition on partial pressure of ammonia and hydrogen is concerned. The rate of decomposition on this pure iron catalyst at about 400° is practically independent of the partial pressure of ammonia and proportional to a power of H_2 varying between $+2$ and -0.6. The measurements made on this catalyst may be well summed up by saying that the kinetics in the range 380–430° appear in general to be characteristic of regions BC or CD. As regards possible formation of —NH or —NH_2 on its surface catalyst 973 is intermediate between catalyst 954 and catalyst 931.

Summary

Ammonia decomposition over three iron synthetic ammonia catalysts has been studied—catalyst 931 (1.3% Al_2O_3, 1.59% K_2O), catalyst 954 (10.2% Al_2O_3), catalyst 973 (0.15% Al_2O_3). The kinetics of the reaction over catalyst 931 were found to be very different from those of the reaction over catalysts 954 and 973.

Throughout the range of temperature and gas composition used the rate of the reaction over catalyst 931 is within experimental error proportional to $(P_{NH_3})^{0.6}/(P_{H_2})^{0.85}$. The apparent energy of activation is 45,600 ± 2000 cal.

Within a considerable range of temperature and gas composition the rate of the reaction over catalyst 954 is directly proportional to the partial pressure of hydrogen, indirectly proportional to the partial pressure of ammonia, and the apparent energy of activation is very small. At higher and lower temperatures the kinetics of the reaction more nearly approach those of the reaction over catalyst 931. The reaction kinetics over catalyst 973 are similar to those over catalyst 954.

Possible interpretations of the results are given.

BELTSVILLE, MARYLAND RECEIVED AUGUST 12, 1941

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Ionization Constant of Propionic Acid in Dioxane–Water Mixtures

BY HERBERT S. HARNED AND THOMAS R. DEDELL[1]

The ionization constants of formic, acetic acids and water in dioxane–water mixtures have been determined from 0 to 50° by means of cells without liquid junction.[2] From the electromotive forces of the cells

$$H_2 \mid HP\ (m_1),\ NaP\ (m_2),\ NaCl\ (m_3),\ \text{Dioxane}\ (X),\ H_2O\ (Y) \mid AgCl\text{–}Ag$$

we have determined the ionization constant of propionic acid (HP) in these media over the same temperature range. From these results the free energy, heat content and entropy of ionization have been calculated.

In addition to these measurements of propionic acid solutions, we have summarized all our determinations of the ionization constants of formic, acetic acids and water in the dioxane–water mixtures by tabulating the constants of a suitable empirical equation. By means of equations derived from this one, all the thermodynamic functions which accompany the ionization processes may be computed.

Experimental Results

Three kilograms of Eastman Kodak Co. propionic acid was purified by fractional distillation in an all-glass column still. The final fraction of 400 g. distilled within 0.05°.

A solution of about four moles of the acid and a liter of water was prepared. The exact molality of this solution was determined by weight titration against standardized sodium hydroxide. The titrations checked to within 0.02%. The number of moles of propionic acid remaining in the solution was calculated and about half as many moles of standardized sodium hydroxide was added.

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(1) This communication contains material from a dissertation presented by Thomas R. Dedell to the Graduate School of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1941.

(2) A complete bibliography is given in connection with Table III of this communication.

Sufficient dry sodium chloride was then introduced so that the molalities of the sodium propionate and chloride were equal. The final molality, m_{HP}, of the propionic acid was 0.84759. The molalities of the other components were: $m_{NaCl} = m_{NaP} = 1.00244\ m_{HP}$. The molality of the acid in this buffer solution was known to within 0.05%. All other solutions were made by dilution of this stock solution with suitable amounts of dioxane and water.

The cell technique has been described carefully by others[3] and no further remarks are required. It will be sufficient to state that all the usual precautions were taken to ensure the accuracy of the results. The reproducibility of the cells was within ± 0.05 mv.

TABLE I

Constants of Equation (1), $E = E_{25} + a(t - 25) + b(t - 25)^2$, where E is Electromotive Force of the cell: H_2 | HP (m_1), NaP (m_2), NaCl (m_3), Dioxane (X), Water (Y) | AgCl – Ag. X = % dioxane by weight. $m_2 = m_3 = 1.00244\ m_1$; temperature range from 0 to 50°.

m_1	E_{25}[a]	ΔE_{25}[b]	$a \times 10^4$[a]	$\Delta a \times 10^4$	$-b \times 10^7$[c]	ΔA[b]
			$X = 20$			
0.00539	0.66054	−0.01	7.82	+0.11	−3.60	0.06
.01124	.64169	+ .05	7.21	− .07	8.66	.04
.01479	.63466	− .07	6.99	+ .01	6.22	.05
.02052	.62628	+ .07	6.72	.00	7.33	.06
.02354	.62277	− .04	6.61	+ .03	5.11	.06
.02790	.61842	+ .09	6.47	− .09	14.80	.09
.02999	.61658	− .11	6.41	− .02	5.00	.09
.04248	.60770	+ .02	6.12	+ .04	6.22	.08
			$X = 45$			
0.01320	0.66222	−0.08	5.66	0.00	2.4	0.02
.01630	.65679	+ .01	5.46	.00	1.6	.02
.01964	.65199	+ .10	5.29	+ .02	2.3	.08
.02230	.64871	− .05	5.17	+ .06	4.0	.12
.02402	.64680	+ .08	5.09	.00	4.0	.07
.03210	.63931	.00	4.83	.00	1.5	.03
.03545	.63675	− .12	4.73	− .12	6.6	.13
.04260	.63199	− .02	4.57	− .05	3.6	.07
.04348	.63146	+ .02	4.55	− .05	...	.28
.05011	.62779	+ .01	4.40	.00	3.7	.06
.05177	.62694	− .06	4.37	.00	3.5	.11
.05789	.62405	+ .05	4.28	− .02	0.0	.09
			$X = 70$			
0.01433	0.68177	+0.02	3.35	0.00	2.00	0.07
.02136	.67122	− .05	2.98	− .03	2.60	.04
.02288	.66939	+ .09	2.92	− .03	2.00	.09
.02972	.66238	− .10	2.68	.00	2.05	.16
.03532	.65772	.00	2.52	− .10	2.60	.09
.04103	.65363	.00	2.39	.00	1.00	.04
.05532	.64535	+ .02	2.11	+ .07	1.66	.10
			$X = 82$			
0.01936	0.67513	−0.07	1.97	−0.01	0.0	0.09
.02417	.66922	+ .12	1.80	.00	.0	.08
.03581	.65863	− .07	1.49	+ .01	.0	.05
.04828	.65042	+ .02	1.27	− .01	.0	.10

[a] Smoothed. [b] Millivolts. [c] Since the contribution of the term involving b is small, −6, −3.6, −2, and 0, each multiplied by 10^{-7}, were used for b for the 20, 45, 70 and 82% mixtures, respectively.

For each molality, the electromotive forces, corresponding to one atmosphere hydrogen pressure, have been expressed by the equation

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

Table I contains the constants of this equation derived by a graphical method.[4] The values of E_{25} given in this table were smoothed by suitable plots against electrolyte concentration. The values of the empirical constant, a, were also smoothed concentration-wise. ΔE_{25} is the difference between observed and smoothed values of E_{25} and Δa represents the difference between the smoothed and unsmoothed values of a. We note that the values of b are very small ($\sim 10^{-7}$) and vary irregularly with concentration. Sufficient accuracy is obtained if the values given in the note to the table are employed. The last column contains the average deviations in millivolts of the differences between the original electromotive forces and those computed by equation (1).

Ionization Constants

The ionization constant was evaluated from the equation for the cell

$$\frac{F}{2.303RT}(E - E_0') + \log\frac{m_{HP}m_{Cl}}{m_P} = -\log K - \log\frac{\gamma_{Cl}\gamma_{HP}}{\gamma} \equiv -\log K' \qquad (2)$$

by plotting the left side, or $-\log K'$, against ionic strength and extrapolating to zero concentrations.[5] In this equation, E_0' is the standard potential of the cell, E, its electromotive force and γ and m are the activity coefficients and molalities of the species denoted by subscripts. Propionic acid is sufficiently weak to render unnecessary the corrections ($m_{HP} = m_1 - m_H$; $m_P = m_2 + m_H$) for the hydrogen ion produced by the dissociation of the

TABLE II

IONIZATION CONSTANTS

t	$X = 0$ $K_A \times 10^5$	$X = 20$ $K_A \times 10^6$	$X = 45$ $K_A \times 10^7$	$X = 70$ $K_A \times 10^9$	$X = 82$ $K_A \times 10^{11}$
0	1.274	3.175	2.641	2.299	...
5	1.305	3.267	2.713	2.364	3.797
10	1.326	3.337	2.764	2.410	3.917
15	1.336	3.385	2.796	2.439	3.966
20	1.338	3.412	2.808	2.450	3.946
25	1.336	3.417	2.801	2.444	3.860
30	1.326	3.403	2.776	2.422	3.716
35	1.310	3.370	2.734	2.386	3.524
40	1.280	3.319	2.677	2.336	3.293
45	1.257	3.252	2.607	2.274	3.035
50	1.229	3.172	2.526	2.202	...

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(3) Harned and Morrison, *Am. J. Sci.*, **33**, 162 (1937); THIS JOURNAL, **58**, 1902 (1936); Harned and Done, *ibid.*, **63**, 2579 (1941).

(4) Harned and Nims, *ibid.*, **54**, 423 (1932).

(5) Harned and Ehlers, *ibid.*, **54**, 1350 (1932).

TABLE III

CONSTANTS OF EQUATIONS (3) TO (10)

X = Weight per cent. of organic solvent

X	A^*	D^*	C^*	A'	D'	C'	T_θ	$-\log K_\theta$
			Water in Dioxane–Water Mixtures[10]					
0	4470.99	6.0875	0.01706	20454.96	27.8506	0.078050	511.9	11.3796
20	4596.78	6.3108	.018487	21030.45	28.8722	.084577	498.7	12.1260
45	4641.08	5.7231	.019784	21233.13	26.1834	.090513	484.3	13.4414
70	4377.47	2.2289	.018116	20027.10	10.1973	.082882	491.6	15.5815
			Formic Acid in Dioxane–Water Mixtures[11]					
0	1342.85	5.2743	.015168	6143.59	24.1301	.069395	297.5	3.7519
20	1339.04	5.0628	.015983	6126.17	23.1626	.072917	289.8	4.1766
45	1333.79	4.6393	.017634	6102.16	21.2248	.080676	275.0	5.0602
70	1181.65	1.9920	.016922	5406.09	9.1135	.077419	264.2	6.9513
82	3006.85	13.2110	.040005	13755.07	60.4408	.18302	274.1	8.7232
			Acetic Acid in Dioxane–Water Mixtures[12]					
0	1170.48	3.1649	.013399	5354.99	14.4795	.061301	295.6	4.7555
20	1423.45	4.2934	.016136	6512.34	19.6425	.073822	297.0	5.2917
45	1568.31	4.5387	.018736	7175.08	20.7650	.085718	289.3	6.3027
70	1549.12	2.5194	.018933	7087.29	11.5264	.086619	286.0	8.3119
82	3763.40	16.0925	.045641	17217.71	73.6238	.208809	287.2	10.1194
			Propionic Acid in Dioxane–Water Mixtures[13]					
0	1213.26	3.3860	.014055	5550.71	15.4911	.064302	293.8	4.8729
20	1356.57	3.67038	.015384	6206.67	16.7930	.070385	297.0	5.4662
45	1480.12	3.52870	.017163	6771.94	16.1447	.078525	293.7	6.5516
70	1508.10	1.65390	.017466	6879.96	7.5670	.079914	293.8	8.6112
82	3680.11	15.05723	.044030	16837.48	68.8908	.20145	289.1	10.4015
			Acetic Acid in Methanol–Water Mixtures[14]					
10	1417.19	4.5806	.015874	6483.70	20.9564	.072624	298.8	4.9055
20	1572.21	5.3447	.017279	7192.92	24.4522	.079052	301.7	5.0796

acid. The values of E_0' required for the calculation were derived from the equations of Harned, Morrison, Walker, Donelson and Calmon.[6] The values of the ionization constants are given in Table II, which also includes the results in pure water obtained by Harned and Ehlers.[7]

In a careful survey of the errors involved in a similar determination of the ionization constant of formic acid, Harned and Done concluded that the gross errors in log K were of the order of 0.35, 0.6, 1.3 and possibly 10% in the 20, 45, 70 and 82% dioxane–water mixtures, respectively. These are the errors which may be assigned to the results in Table II. For the chief sources of these errors we refer to the discussion of Harned and Done.[8]

Calculations of Ionization Constants and Related Thermodynamic Functions of Water, Formic, Acetic and Propionic Acids in Dioxane–Water Mixtures.—For these calculations, we have employed the equation

$$\log K = -A^*/T + D^* - C^*T \qquad (3)$$

of Harned and Robinson[9] from which the free energy, ΔF^0, heat content, ΔH^0, heat capacity, ΔC_p^0, and entropy, ΔS^0, of the ionization reactions may be computed by the relations

$$\Delta F^0 = A' - D'T + C'T^2 \qquad (4)$$

$$\Delta H^0 = A' - C'T^2 \qquad (5)$$

$$\Delta C_p^0 = -2C'T \qquad (6)$$

$$\Delta S^0 = D' - 2C'T \qquad (7)$$

where

$$\begin{aligned} A' &= 2.303RA^* \\ D' &= 2.303RD^* \\ C' &= 2.303RC^* \end{aligned} \qquad (8)$$

The maximum value of the ionization constant, K_θ, and the temperature of the maximum, T_θ, are given by

$$\log K_\theta = D^* - 2\sqrt{C^*A^*} \qquad (9)$$

$$T_\theta = \sqrt{A^*/C^*} \qquad (10)$$

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[6] Harned, Morrison, Walker, Donelson and Calmon, THIS JOURNAL, **61**, 49 (1939).

[7] Harned and Ehlers, *ibid.*, **55**, 2379 (1933).

[8] Harned and Done, *ibid.*, **63**, 2579 (1941).

[9] Harned and Robinson, *Trans. Faraday Soc.*, **36**, 973 (1940).

[10] Harned and Robinson, *ibid.*, **36**, 973 (1940); Harned and Fallon, THIS JOURNAL, **61**, 2374 (1939).

[11] Harned and Embree, *ibid.*, **56**, 1042 (1934); Harned and Done, *ibid.*, **63**, 2579 (1941).

[12] Harned and Ehlers, *ibid.*, **55**, 2179 (1933); Harned and Kazanjian, *ibid.*, **58**, 1912 (1936); Harned and Fallon, *ibid.*, **61**, 2377 (1939).

[13] Harned and Ehlers, *ibid.*, **56**, 2379 (1934); this investigation.

[14] Harned and Embree, *ibid.*, **57**, 1669 (1935).

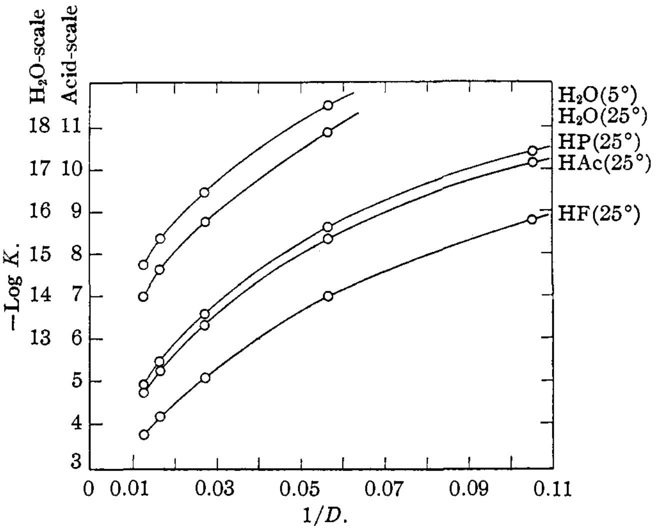

Fig. 1.—Ionization constants as a function of the dielectric constant in dioxane–water mixtures: HF, formic acid; HAc, acetic acid; HP, propionic acid.

The empirical constants of these equations for water, formic, acetic and propionic acids in dioxane–water mixtures, and acetic acid in methanol–water mixtures are given in Table III. The last two columns contain T_θ and $-\log K_\theta$. The sources of the data are given at the bottom of the table. We are indebted to Dr. Robert A. Robinson of the University of New Zealand for computations for water and acetic acid in both the dioxane- and methanol–water mixtures.

In Table IV, values of the thermodynamic functions at 25° computed by these equations are compiled. The uncertainty of ΔF^0 in the 0, 20, 45 and 70% dioxane solutions is estimated to be about 2, 2, 4, and 10 cal., respectively. The entropy in these solutions is known to within 0.3 cal. The errors in the estimation of ΔH^0 and ΔC_p^0 are of the order of 100 cal. and 3 cal., respectively. The results in the 82% dioxane solutions are uncertain due to the difficulty of obtaining accurate values of E_0'. No accurate estimate of their reliability is possible at present.

TABLE IV

ΔF^0, ΔH^0, ΔC_p^0 AND ΔS^0 OF IONIZATION AT 25° IN CALORIES

X = % Dioxane by Weight

X	ΔF^0	ΔH^0	ΔC_p^0	ΔS^0
		Water		
0	19089	13519	− 46.5	− 18.7
20	19940	13515	− 50.4	− 21.5
45	21470	13190	− 54.0	− 27.8
70	24353	12662	− 49.4	− 39.2
		Formic Acid		
0	5117	− 23	− 41.7	−17.6
20	5701	359	− 43.4	−17.92
45	6944	1067	− 48.1	−19.72
70	9569	1474	− 46.2	−27.16
82	12002	2509	−109.1	−31.84
		Acetic Acid		
0	6486	− 92	− 36.5	−22.1
20	7217	− 52	− 44.0	−24.4
45	8602	− 442	− 51.1	−30.3
70	11348	− 610	− 51.7	−40.1
82	13827	−1338	−124.5	−50.8
		Propionic Acid		
0	6647	− 163	− 38.3	−22.8
20	7455	− 48	− 42.0	−25.5
45	8937	− 206	− 46.8	−30.7
70	11746	− 201	− 47.6	−40.1
82	14203	−1064	−120.1	−51.2

Theoretical Considerations

In Fig. 1, $-\log K$ at 25° is plotted against the reciprocal of the dielectric constant. As pointed out by Harned,[15] these plots are not linear, and therefore Born's equation is not valid. This result is not unexpected since large contributions due to molecular interaction may occur in addition to those caused by Coulombic forces.

Gurney[16] has suggested a theory for the temperature variation of ionization which has been developed in suitable manner by Baughan.[17] Let the total free energy, ΔF^0, be separated into a chemical, $\Delta F^0_{(D=\infty)}$, and an electrical part, ΔF^0 (El)

$$\Delta F^0 = \Delta F^0_{(D=\infty)} + \Delta F^0(\text{El}) \qquad (11)$$

If we assume that electrical part is given by Born's equation and employ the relation, $\Delta F^0 = -RT \ln K$, relating the standard free energy with the ionization constant

$$-\ln K = -\ln K_{(D=\infty)} + \frac{e^2}{2DRT}\left(\frac{1}{r_+} + \frac{1}{r_-}\right) \qquad (12)$$

for a univalent electrolyte. Utilizing the thermodynamic equations

$$\frac{\partial \ln K}{\partial T} = \frac{\Delta H^0}{RT^2}$$

and

$$\frac{\partial \ln K_{(D=\infty)}}{\partial T} = \frac{\Delta H^0_{(D=\infty)}}{RT^2} \qquad (13)$$

we obtain upon differentiating equation (12)

$$\Delta H^0 = \Delta H^0_{(D=\infty)} + C\left[\frac{1}{D}\left(1 + T\frac{\partial \ln D}{\partial T}\right)\right] \qquad (14)$$

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(15) Harned, *J. Phys. Chem.*, **43**, 275 (1939).

(16) Gurney, *J. Chem. Phys.*, **6**, 499 (1938).

(17) Baughan, *ibid.*, **7**, 951 (1939).

where

$$C = \frac{e^2}{D}\left(\frac{1}{r_+} + \frac{1}{r_-}\right) \quad (15)$$

The validity of equation (14) as applied by Baughan rests upon two factors. It presupposes the correctness of Born's equation over the temperature range. From 0 to 60° in water this involved a change in D from 88 to 67. The second factor involves an assumption regarding the variation of $\Delta H^0_{(D=\infty)}$ with temperature. From the recent measurements of Everett and Wynne-Jones[18] of the ionization of the ammonium ion, and of Pedersen,[19] who determined the ionization constants of the anilinium and *o*-chloroanilinium ion, it appears that for these isoelectric dissociations, ΔC^0_p is zero and ΔH^0 is independent of the temperature. More recent studies,[20] however, reveal that the mono-, di- and trimethylammonium ion dissociations are accompanied by changes in heat capacities of 7, 20 and 41 cal., respectively, so that the temperature independence of $\Delta H^0_{(D=\infty)}$ may be far from valid. In spite of the doubtful nature of this assumption, Baughan succeeded in obtaining results which lead to the right order of magnitude of the ionic radii.

According to equation (14), a plot of ΔH^0 against $\left(1 + T\frac{\partial \ln D}{\partial T}\right)$ should be a straight line with a slope C and an intercept $\Delta H^0_{(D=\infty)}$. Plots of our values of ΔH^0 using Åkerlöf and Short's[21] dielectric constant data are nearly straight but all show slight curvatures in the same direction. From the values of C estimated from the slopes, values of the mean radius, r, defined by

$$\frac{2}{r} \equiv \frac{1}{r_+} + \frac{1}{r_-} \quad (16)$$

were determined. These are recorded in Table V.

TABLE V

VALUES OF MEAN IONIC RADII DERIVED BY MEANS OF EQUATION (14)

X = % by weight of dioxane

X	H_2O	HCOOH	CH_3COOH	CH_3CH_2-COOH
0	0.61	0.68	0.77	0.74
20	0.86	1.00	0.99	1.04
45	1.51	1.70	1.60	1.75
70	3.62	3.88	3.47	3.76
82	..	2.38	2.09	2.17

Although these values of r are of the right order of magnitude, no convincing conclusions can be obtained directly from them. In water they seem to be too small and in 70% dioxane–water mixtures they are too large. Indeed, their variation with change in solvent will be difficult to explain.

Summary

1. The electromotive forces of the cell $H_2|$ HP (m_1), NaP (m_2), NaCl (m_3)|AgCl – Ag have been determined in dioxane–water mixtures containing 20, 45, 70 and 82% dioxane. Measurements were made at 5° intervals from 0 to 50° for the first three mixtures and from 5 to 45° for the 82% dioxane mixture.

2. From these results, the ionization constant of propionic acid was evaluated.

3. The ionization constants of formic, acetic, propionic acids and water in dioxane–water mixtures have been expressed by the equation log $K = -(A^*/T) + D^* - C^*T$. From the constants of this equation and those of equations (5) to (10) given in Table III, all the thermodynamic functions of the ionization processes may be computed. Values of the free energy, heat content, heat capacity and entropy changes at 25° accompanying ionization are given in Table IV.

4. The results have been discussed in relation to the theory proposed by Baughan. Doubt is raised concerning both the validity of the Born equation and the assumpion that the non-electrostatic part of the heat content of ionization is independent of the temperature.

NEW HAVEN, CONN. RECEIVED SEPTEMBER 17, 1941

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(18) Everett and Wynne-Jones, *Proc. Roy. Soc.* (London), **169A**, 190 (1938).

(19) Pedersen, *K. danske vidensk. Selsk. Skr.*, **14**, 9 (1937); **15**, 3 (1937).

(20) Everett and Wynne-Jones, *Trans. Faraday Soc.*, **35**, 1380 (1939).

(21) Åkerlöf and Short, THIS JOURNAL, **58** 1241 (1936).