

assumptions that probabilities of removing atoms are equal to those found in methane. Unfortunately, one must base such a derivation on the values derived from CHD_3 that are considered least reliable experimentally.

V. Conclusions

The sensitivities of CH_4 and CD_4 differ by about 2 percent and are probably equal within the experimental uncertainty. The total ionization is apparently the same for CH_4 , CH_3D , and CH_2D_2 . The low value for CHD_3 is not significant in view of the uncertainty in this spectrum. The difference in the total ionization of CH_4 and CD_4 , however, is greater than the estimated error; and since the number of dissociation processes remains the same, the difference is probably a result of the lower probability of dissociating C-D bonds.

Although our experimental results for CH_3D are in good agreement with Turkevich et al. and with Evans, Bauer, and Beach, the different authors have used somewhat different assumptions in the interpretation of results. Although the assumptions used by

Evans, Bauer, and Beach lead to nearly the same results in CH_3D , their assumptions did not seem to be generally applicable to the three spectra CH_3D , CH_2D_2 , and CHD_3 , necessitating the different approach used in this work.

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First Dissociation Constant of Succinic Acid from 0° to 50° C and Related Thermodynamic Quantities

By Gladys D. Pinching and Roger G. Bates

The first dissociation constant, K_1 , of succinic acid was determined at intervals of 5 degrees from 0° to 50° C from measurements of the electromotive force between hydrogen and silver-silver-chloride electrodes in cells without liquid junction. In order to reduce the correction for "overlapping" of the two acid groups, which are of nearly equal strengths, the 10 solutions studied contained twice as much succinic acid as acid succinate ion. The residual correction of about 0.02 in $\log K_1$ was made with the aid of values of the second dissociation constant from an earlier determination.

The first dissociation constant between 0° and 50° can be expressed by

$$-\log K_1 = 1206.25/T - 3.3266 + 1.011697T,$$

where T is the absolute temperature. The changes of free energy, heat content, entropy, and heat capacity for the first dissociation step of succinic acid in the standard state were calculated from the dissociation constant and its temperature coefficient.

I. Introduction

A determination of the second dissociation constant of succinic acid from 0° to 50° was recently reported by the authors [1].¹ The two acid groups of this dicarboxylic acid are of nearly equal strengths, and there is considerable overlapping, or simultaneous dissociation. Hence, it was necessary to estimate the first dissociation constant, K_1 , in order to compute the ionic concentrations required for an accurate determination of the second dissociation constant, K_2 . Values of K_1 were therefore calculated from electromotive-force measurements of solutions of sodium acid succinate with added sodium chloride

from 0° to 50° by means of a determination of the product of the two constants [2].

Although adequate for correcting the determination of K_2 , these values of $\log K_1$ were estimated to have an uncertainty of ± 0.01 . Hence, it is doubtful if the earlier results for K_1 are of sufficient accuracy to warrant the calculation of the heat-content and entropy changes that are of considerable theoretical interest. It seemed desirable to undertake an accurate redetermination of the first dissociation constant in order to obtain reliable information concerning the thermodynamic quantities associated with the first dissociation step.

Ten mixtures of hydrochloric acid and sodium acid succinate were prepared, each containing the

¹ Figures in brackets indicate the literature references at the end of this paper.

TABLE I. Electromotive force of cell I from 0° to 50°

m	Temperature, °C										
	0	5	10	15	20	25	30	35	40	45	50
0.09959	0.50441	0.50672	0.50893	0.50818	0.50929	0.51035	0.51145	0.51250	0.51351	0.51448	0.51537
.09982	.50686	.50812	.50940	.51057	.51172	.51290	.51399	.51503	.51620	.51715	.51804
.09929	.50964	.51107	.51242	.51375	.51500	.51622	.51740	.51858	.51968	.52073	.52165
.07684	.51280	.51414	.5154	.51697	.51831	.51954	.52078	.52182	.52302	.52408	.52523
.05036	.52112	.52272	.52424	.52574	.52725	.52861	.52999	.53133	.53262	.53392	.53500
.04983	.52118	.52288	.52441	.52592	.52735	.52888	.53022	.53160	.53292	.53418	.53547
.02977	.53364	.53555	.53737	.53913	.54086	.54248	.54410	.54568	.54724	.54878	.55024
.019875	.54350	.54558	.54751	.54945	.55131	.55320	.55498	.55670	.55836	.56007	.56171
.015114	.55020	.55243	.55446	.55635	.55819	.56004	.56183	.56350	.56522	.56684	.56849
.009890	.56023	.56255	.56499	.56728	.56963	.57174	.57383	.57593	.57797	.57991	.58190

latter at one and one-half times the molality, m , of the former, and the electromotive force of the cell,

Pt; $H_2(g, 1 \text{ atm})$, NaH succinate (1.5 m), HCl (m),
AgCl; Ag, (I)

was measured at intervals of 5 degrees from 0° to 50°. The first dissociation constant of succinic acid was calculated from the experimental data. Corrections were applied for the amount of bivalent succinate ion formed in the solutions by dissociation of the acid succinate ion. The changes of free energy, heat content, entropy, and heat capacity for the dissociation of 1 mole of succinic acid in the standard state were evaluated from the dissociation constant and its temperature coefficient.

II. Experimental Procedures and Results

The stock solution of hydrochloric acid was prepared by dilution of a portion of redistilled acid. The mean deviation of five gravimetric analyses from the mean molality was less than 0.02 percent.

Sodium acid succinate, prepared from reagent-grade succinic acid and a standard solution of sodium hydroxide, was recrystallized from water with the addition of sufficient sodium hydroxide to bring the salt to the proper composition. After samples of the salt were dried at 110°, they were found to neutralize 100.03 percent of the theoretical amount of standard alkali. The titration was carried to pH 8.7 with the use of phenolphthalein and a color standard.

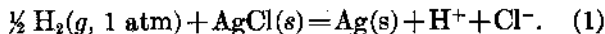
Nitrogen was passed through each buffer solution for 2 hr to remove dissolved oxygen. The cells were filled and placed in the water thermostat where they were kept at 25° for about 6 hr to insure initial equilibrium. The emf measurements from near 0° to 25° were made on the second day, and from 25° to 50° on the third, after which the temperature of the thermostat was lowered to 25° for a final measurement. The average difference between the initial and final emf of the 10 cells was less than 0.08 mv, or 0.0013 in $\log K_1$. The electrodes were prepared in the same manner as for the determination of the second dissociation constant [1].

Each emf value, E , given in table 1 is the mean of the potentials between two pairs of electrodes in the

same cell. The molality, m , of hydrochloric acid appears in the first column.

III. Calculation of the Dissociation Constant

Withdrawal of electrical energy from cell I causes the following electrochemical reaction to take place:



The initial, reversible potential of the cell depends upon the extent to which the system is displaced from the equilibrium condition, that is, upon the difference between the reaction quotient, Q , and equilibrium constant, Q_e , for reaction 1. If the usual conventions regarding the standard state with respect to which activity, a , is measured are observed, we may write

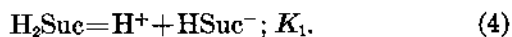
$$Q = a_H a_{Cl}, \quad (2)$$

and

$$\Delta F = RT \ln Q/Q_e = \Delta F^\circ + RT \ln Q. \quad (3)$$

In eq 3, ΔF is the molal free-energy change in reaction 1 for any particular state of the system and ΔF° is the corresponding quantity for unit activities of reactants and products.

Inasmuch as the solution is well buffered, the hydrogen ion formed by reaction 1 is largely utilized in converting acid succinate ion ($HSuc^-$) into molecular succinic acid (H_2Suc). The equilibrium between these constituents of the solution is the first dissociation of succinic acid:



The activity of hydrogen ion is fixed by the activities of the two succinate species and by the first dissociation constant, K_1 , of succinic acid. Hence, Q can be written

$$Q = K_1 a_{H_2Suc} a_{Cl} / a_{HSuc^-}. \quad (2a)$$

As only electrical work is of concern here,

$$\Delta F = -EF, \quad (5)$$

and

$$\Delta F^\circ = -E^\circ F. \quad (5a)$$

In eq 5a, E° is the standard potential of reaction 1 [3, 4]², and F is the faraday. Substitution of eq 2a, 5, and 5a in eq 3 and rearranging gives

$$-\log K_1 = \left[\frac{(E - E^\circ)F}{2.3026RT} + \log m_{Cl} \right] + \log \frac{m_{H_2Succ}}{m_{HSucc}} + \log \frac{f_{H_2Succ} f_{Cl}}{f_{HSucc}} \quad (6)$$

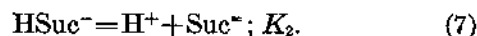
where f is an activity coefficient on the molal scale. In cell I, $m_{Cl} = m$.

If eq 6 is compared with the mass-law expression for the first dissociation (eq 4) in logarithmic form, it is seen that the portion of eq 6 enclosed in brackets actually represents the value of $-\log(f_H f_{Cl} m_H)$ in the particular solution for which the emf, E , was measured. For convenience, this experimental quantity will be called pWH .

The last term of eq 6 cannot be evaluated exactly without a knowledge of K_1 . However, in agreement with the predictions of the Hückel equation [5], similar activity-coefficient terms for a number of weak monobasic acids have been found to be small and to vary linearly with ionic strength. By definition, this term is zero at infinite dilution. Hence, $\log K_1$ at zero ionic strength was evaluated by extrapolation of $\log K_1'$, the value of $\log K_1$ calculated by eq 6 with the last term set equal to zero.

The computation of the next to the last term on the right of eq 6 may be quite difficult for systems with two or more overlapping equilibria. The difficulty is aggravated if one group is moderately strong and the concentration of hydrogen ion is consequently an appreciable fraction of the ionic strength. Although the ratio of K_1 to K_2 for succinic acid is only 26 and overlapping is considerable, neither dissociation constant exceeds 10^{-4} , and the hydrogen-ion correction was readily evaluated.

When sodium acid succinate is dissolved in a solution of hydrochloric acid, as in the preparation of the buffer solutions used in this study, the reaction between hydrogen ion and acid succinate ion does not go to completion because of the small (but appreciable) dissociation of the molecular succinic acid formed (eq 4). Furthermore, the second dissociation constant is not small enough, nor the hydrogen-ion concentration large enough, to prevent the dissociation of a part of the acid succinate ion,



It can be shown that the molalities of succinic acid and acid succinate ion remaining at equilibrium are given by the following equations:

$$m_{H_2Succ} = m - m_H + m_{Succ^-}, \quad (8)$$

and

$$m_{HSucc^-} = 0.5 m + m_H - 2 m_{Succ^-}. \quad (9)$$

The concentrations of the constituents of the cell solutions were so chosen that the concentration of

succinic acid was about twice that of the acid succinate ion. In this way overlapping, as evidenced by the magnitude of m_{Succ^-} , was reduced. It should be emphasized, however, that this device is not always advantageous, for m_H , which usually cannot be measured accurately, is inevitably increased.

Values of m'_H , a quantity that approaches the true hydrogen-ion molality, m_H , as the ionic strength decreases, were computed from pWH by

$$-\log m'_H = \text{pWH} - 2A\sqrt{\mu}/(1 + 7B\sqrt{\mu}). \quad (10)$$

The coefficient 7 in the denominator of the last term is the value found most suitable to describe the activity-coefficient term in mixtures of primary and secondary sodium succinates [1], and A and B are constants of the Debye-Hückel theory.

An exact expression for m_{Succ^-} is the following:

$$m_{Succ^-} = K_2 m_{HSucc^-} (\text{antilog pWH}) (f_{HSucc} f_{Cl} / f_{Succ^-}). \quad (11)$$

If the activity coefficients are again estimated by the Debye-Hückel equation, an expression for m'_{Succ^-} is obtained:

$$\log m'_{Succ^-} = \log K_2 + \log m_{HSucc^-} + \text{pWH} + 2A\sqrt{\mu}/(1 + 7B\sqrt{\mu}). \quad (12)$$

Inasmuch as the dissociation constant is obtained by extrapolation to infinite dilution where uncertainties in the estimation of activity coefficients disappear, m'_H and m'_{Succ^-} were used for m_H and m_{Succ^-} in eq 8 and 9. The ionic strength is given by

$$\mu = 1.5m + m'_H + m'_{Succ^-}. \quad (13)$$

The ionic concentrations required in eq 6 were accordingly calculated by eq 8, 9, 10, and 12 with the aid of the values of K_2 obtained in the earlier study [1]. The ionic strength needed to compute m'_H and m'_{Succ^-} was obtained by arithmetic approximations. Both acid groups of succinic acid are fairly weak, and m_H was only 1.6 percent of m for the most dilute solution studied. The extent of overlapping was greatest for the most concentrated solution, in which m'_{Succ^-} amounted to about 1.5 percent of m .

Figure 1 illustrates the effect of the K_2 correction and of the method of estimating the activity coefficients on the determination of K_1 . The circles and upper solid line (drawn by inspection) represent the final corrected values of $\text{p}K_1'$ ($-\log K_1'$). If the correction for bivalent succinate ion had been omitted, the lower solid line would have resulted, and the value of $\text{p}K_1$ found would have been about 0.02 unit too low. If 4 had been chosen instead of 7 as the coefficient of the $B\sqrt{\mu}$ term in the denominator of eq 10 and 12, the extrapolation would have followed the broken line. However, the two upper lines converge satisfactorily, and the value of $\text{p}K_1$ at zero ionic strength would not have been altered.

The slopes, $-\beta$, of the plots of $\text{p}K_1'$ versus μ were measured for each temperature and $\beta\mu$ added to $\text{p}K_1'$

² Reference [4] lists E° and $2.3026RT/F$ in absolute volts.

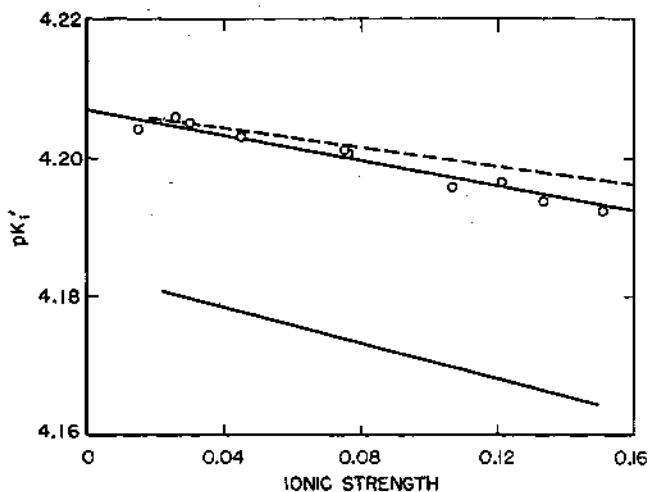


FIGURE 1. Extrapolation of pK_1 to zero ionic strength at 25° .

The broken line represents the best fit of the experimental values of pK_1 if 4 is used instead of 7 in the denominator of eq 10 and 12. Similarly, the position of the lower solid line illustrates the effect of omitting the correction for overlapping of the first and second acid groups.

computed from each experimental point. The resulting values of pK_1 were averaged. The mean pK_1 is listed in the fourth column of table 2, together with the average deviation of the 10 individual values from the mean at each temperature. The uncertainty in $\log K_1$ is estimated to be less than ± 0.003 unit. The dissociation constant is given in the last column of the table. The values of $\log K_2$ used to compute the correction for overlapping are given in the second column, and $\log K_1$ derived from a measurement of K_1K_2 in the earlier study [1] appears in the third. The distribution of the individual results for pK_1 on either side of the mean at 0° , 25° , and 50° is shown in figure 2.

Earlier determinations of the first dissociation constant are summarized in table 3. No recalculation of any of the data has been attempted. Unfortunately, Jones and Soper [23], who also used the hydrogen-silver-chloride cell but a different method of calculation, do not list their emf values. Hence,

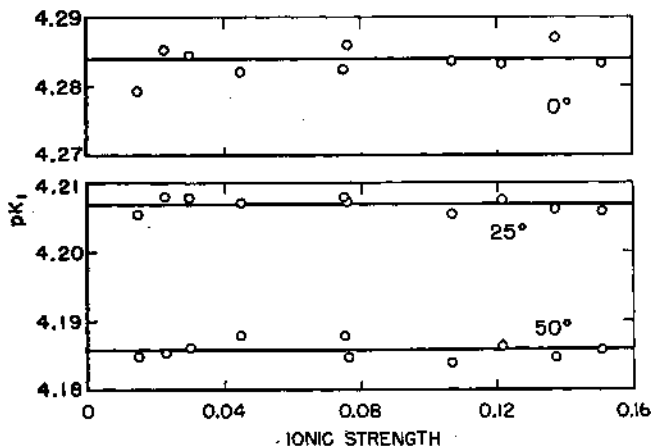


FIGURE 2. Distribution of values of pK_1 at 0° , 25° , and 50° .

TABLE 2. Values of $\log K_2$, $\log K_1$, and K_1 from 0° to 50°

Temperature °C	$-\log K_2$ (ref. 1)	$-\log K_1$ (ref. 1)	$-\log K_1$	$K_1 \times 10^6$
0	5.674	4.22 ₆	4.2845 ± 0.0018	5.20
5	5.661	4.26 ₅	4.2631 ± 0.0011	5.46
10	5.649	4.24 ₇	4.2449 ± 0.0008	5.70
15	5.643	4.23 ₃	4.2316 ± 0.0008	5.88
20	5.639	4.22 ₃	4.2176 ± 0.0008	6.07
25	5.636	4.20 ₆	4.2066 ± 0.0009	6.21
30	5.642	4.20 ₆	4.1980 ± 0.0008	6.34
35	5.648	4.19 ₄	4.1914 ± 0.0013	6.45
40	5.654	4.19 ₄	4.1878 ± 0.0012	6.50
45	5.670	4.19 ₆	4.1869 ± 0.0015	6.51
50	5.680	4.18 ₈	4.1863 ± 0.0010	6.52

TABLE 3. Summary of determinations of $\log K_1$

Reference	Method	t	$-\log K_1$
Conductance			
1889, Ostwald [6]		26	4.177
1891, Crum Brown and Walker [7]		25	4.17
1891, Walden [8]		25	4.168
1904, Voerman [9]		26	4.186
		9	4.250
1910, White and Jones [10]		25	4.184
		35	4.181
1916, Büseken and Verkade [11]		26	4.186
1935, Jeffery and Vogel [12]		25	4.179
Reaction rate			
1924, Duboux and Tsamados [24]	Sucrose inversion.	73	4.25
1928, Dawson, Hall, and Key [25]	I ₂ -acetone	25	4.201
Emf, cells with liquid junction			
1924, Auerbach and Smolczyk [13]	Q-cal	20	4.164
1925, Britton [14]	H-cal	18	4.036
1928, Mizutani [15]	H-cal	18, 20	4.09
1928, Simms [16]	H-cal	25	4.195
1928, Koltzoff and Bosch [17]	H-cal	18	4.18
1928, Gane and Ingold [18]	H-cal	25	4.133
1929, Ölander [19]	H-Q; Q at 18°	18	4.22
		50	4.219
1931, Gane and Ingold [20]	H-cal	25	4.193
1934, Ashton and Partington [21]	H-cal	25	4.060
1936, German and Vogel [22]	Q-cal	25	5.196
Emf, cells without liquid junction			
1936, Jones and Soper [23]	H-AgCl	25	4.162
		50	4.135
		74	4.132
		20	4.218
1950, This investigation	H-AgCl	25	4.207
		35	4.191
		50	4.186

* H = hydrogen electrode, Q = quinhydrone, cal = calomel.

the difference of 0.045 at 25° and 0.054 at 50° between the two determinations cannot be explained.

IV. Thermodynamic Functions

By the method of least squares, the following two equations were found to represent the values of $\log K_1$ given in table 2:

$$-\log K_1 = A/T + B + CT = 1206.25/T - 3.3266 + 0.011697T, \quad (14)$$

and

$$-\log K_1 = A^*/T + B^* + C^* \log T$$

$$= 2462.9/T - 47.9882 + 17.755 \log T. \quad (15)$$

The first has the form of the equation proposed by Harned and Robinson [26] to express dissociation constants as a function of temperature. It is based upon the observation that ΔF° is a quadratic function of T , whereas the second equation presupposes that ΔH° is a linear function of T . By differentiation of eq 14 and 15 with respect to temperature, two expressions for the temperature coefficient of $\log K_1$ are obtained:

$$d \log K_1/dT = 1206.25/T^2 - 0.011697, \quad (14a)$$

and

$$d \log K_1/dT = 2462.9/T^2 - 7.7108/T. \quad (15a)$$

The corresponding second derivatives are:

$$d^2 \log K_1/dT^2 = -2412.5/T^3, \quad (14b)$$

and

$$d^2 \log K_1/dT^2 = 7.7108/T^2 - 4925.8/T^3. \quad (15b)$$

The changes of free energy, (ΔF°), heat content (ΔH°), entropy (ΔS°), and heat capacity (ΔC_p°) for the ionization process in the standard state were calculated by the following formulas:

$$\Delta F^\circ = -2.3026RT \log K_1, \quad (16)$$

$$\Delta H^\circ = 2.3026RT^2(d \log K_1/dT), \quad (17)$$

$$\Delta S^\circ = 2.3026R[\log K_1 + T(d \log K_1/dT)], \quad (18)$$

$$\Delta C_p^\circ = 2.3026R[2T(d \log K_1/dT) + T^2(d^2 \log K_1/dT^2)]. \quad (19)$$

The values of these functions at 0°, 25°, and 50° C computed from the two empirical representations of the relationship between $\log K_1$ and T are compared in table 4. Cottrell and Wolfenden [27] have combined their calorimetric data for ΔH° and its temperature coefficient with the dissociation constant found by Jones and Soper [23] to calculate the thermodynamic constants at 25° C. Their results, labeled (C and W) are included in table 4.

The two empirical equations, 14 and 15, evidently lead to appreciably different results for the thermodynamic functions at the extremes of the temperature range. Unfortunately, the only basis for a choice between them is the fit of the "observed" data. The mean departure of the calculated $\log K_1$ from the observed is 0.0005 unit for eq 14 and 0.0011 unit for eq 15. Indeed, eq 14 usually provides the better fit of the observed dissociation constants

TABLE 4. Comparison of thermodynamic functions derived from two different empirical equations (eq 14 and 15) for the variation of $\log K_1$ with T

Equation	ΔF°	ΔH°	ΔS°	ΔC_p°
0° C				
14.....	<i>j mole</i> ⁻¹ 22,407	<i>j mole</i> ⁻¹ 6,384	<i>j deg</i> ⁻¹ <i>mole</i> ⁻¹ -88.6	<i>j deg</i> ⁻¹ <i>mole</i> ⁻¹ -122
15.....	22,417	6,828	-87.1	-148
25° C				
14.....	24,013	3,186	-69.8	-134
15.....	24,007	3,138	-70.0	-148
(C and W)...	* 23,765	2,519	-71.1	-132
50° C				
14.....	25,900	-293	-81.0	-145
15.....	25,908	-553	-81.9	-148

* From the value of K_1 found by Jones and Soper [23].

for weak electrolytes. Hence, eq 14, 14a, and 14b were used to compute the thermodynamic quantities listed in table 5. The estimated uncertainty in ΔF° is 18 j; in ΔH° , 300 j; in ΔS° , 1.0 j; and in ΔC_p° , 15 j.

TABLE 5. Thermodynamic functions for the first dissociation of succinic acid

Temperature	ΔF°	ΔH°	ΔS°	ΔC_p°
°C	<i>j mole</i> ⁻¹	<i>j mole</i> ⁻¹	<i>j deg</i> ⁻¹ <i>mole</i> ⁻¹	<i>j deg</i> ⁻¹ <i>mole</i> ⁻¹
0	22,407	6,384	-88.6	-122
5	22,706	5,767	-69.9	-125
10	23,015	5,138	-63.1	-127
15	23,337	4,499	-65.4	-129
20	23,669	3,848	-67.6	-131
25	24,013	3,186	-69.8	-134
30	24,367	2,513	-72.1	-136
35	24,734	1,828	-74.3	-138
40	25,111	1,132	-76.6	-140
45	25,500	425	-78.8	-142
50	25,900	-293	-81.0	-145

Cottrell and Wolfenden [27] estimated that ΔH° becomes zero at about 45° C. The dissociation constants found by Jones and Soper [23], on the other hand, appear to reach a maximum (and $-\log K_1$ a minimum) between 50° and 74°. The temperature, T_{\min} , at which $-\log K_1$ passes through the minimum is readily calculated in terms of the constants of eq 14 and 15 by setting the first derivative equal to zero. Hence, from eq 14,

$$T_{\min} = A/C, \quad (20)$$

and from eq 15,

$$T_{\min} = 2.3026 A^*/C^*. \quad (21)$$

The data of this investigation place the minimum value of $-\log K_1$ at 47.9° C (eq 20) and 46.2° C (eq 21).

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Effects of Prior Static and Dynamic Stresses on the Fatigue Strength of Aluminum Alloys

By John A. Bennett and James L. Baker

Tests made on specimens of Alclad 24S-T sheet showed that prior static load had a marked effect on the fatigue strength in unidirectional bending when the stress amplitude was relatively small. From tests on bare 24S-T sheet, it was found that a few cycles at a stress amplitude of 17,000 lb/in.² resulted in a large increase in the fatigue life at 20,000 lb/in.² Damage tests for other combinations of stress amplitudes indicated that the damage was nearly a linear function of ratio of the number of cycles at a given stress to the number that would cause failure at that stress. A new design of specimen and a new form of stress versus number of cycles to fracture (*S-N*) diagram are described.

I. Introduction

The phenomenon of fatigue failure in metals remains incompletely understood, despite the extensive research that has been done on the subject. In particular, the mechanism by which a small volume of metal is damaged by repeated stressing until a crack forms may be considered one of the outstanding mysteries in the mechanical behavior of materials. The purpose of the work reported in this paper was to evaluate some of the factors involved in this damaging process by using aluminum alloy specimens. As there appears to be no reliable means of measuring fatigue damage except by a fatigue test, this evaluation was carried out largely by means of tests at two stress levels.

Many investigators have reported experimental data showing the effect of dynamic stressing at one amplitude on the fatigue strength at a second amplitude, but the data for aluminum alloys are not in good agreement. Miner [1]¹ found in testing 24S-T that the damage was proportional to the cycle ratio² within the experimental error. On the other hand,

Stickley [2, 3] reported that the fatigue strength of 17S-T rod could be increased by prestressing at a stress amplitude slightly below the test stress. Likewise, Work & Dolan [4] found an increase in fatigue life due to stressing at small amplitudes. However, Dolan, Richart, and Work [5] found for 17S-T that the fatigue life under gradually varying load cycles was greater when the minor stress amplitude was 18,000 lb/in.² than when it was decreased to 16,000 lb/in.²

These results do not give any consistent picture of the progress of fatigue damage in aluminum alloys, and it was the purpose of this work to evaluate this progress in much the same way that it was done for SAE X4130 steel in the investigation reported in [6].

One of the most interesting phenomena associated with fatigue is the improvement due to understressing. In ferrous materials this improvement increases as the amplitude of the understress approaches the fatigue limit. Aluminum alloys have no fatigue limit, and the effect of understressing is not so marked, but it is known to cause an increase in fatigue strength under certain conditions. It seemed reasonable that during the course of a fatigue test at relatively low stress there must be a reversal in the

¹ Figures in brackets indicate the literature references at the end of this paper.
² Cycle ratio is defined as the ratio of the number of cycles at a given stress amplitude to the number necessary to cause failure at that amplitude. Failure may be defined as either the beginning of a crack or complete fracture.