TABLE I
HEAT CAPACITY OF ACETONE
Set I, Reverse-Flow Calorimeter, 760 mm.

t, °C.	61	75	90	105
T, °K.	334	348	363	378
c_p, cal./g./degree	0.375	0.374	0.380	0.384
C_p, cal./mole/degree	21.8	21.7	22.1	22.3

t, °C.	120	135	155	165
T, °K.	393	408	428	438
c_p, cal./g./degree	0.390	0.398	0.416	0.420
C_p, cal./mole/degree	22.7	23.1	24.2	24.4

Set II, Direct-Flow Calorimeter, 760 mm.

t, °C.	59.4	74.6	99.1	149.4
T, °K.	332.6	347.8	372.3	422.6
c_p, cal./g./degree	0.376	0.374	0.380	0.406
C_p, cal./mole/degree	21.8	21.7	22.0	23.6

ranges 26 to 110° and 27 to 179° by Wiedmann,[7] and 23.9 for the range 129 to 233° by Regnault.[8]
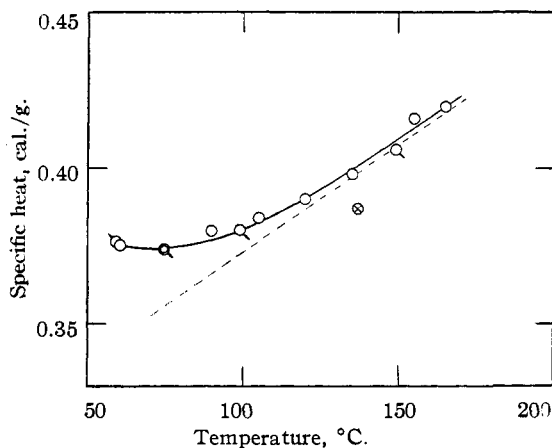

Fig. 1.—Specific heat of acetone: O, set I; ⊶, set II; ⊗, Bennewitz; - - - -, Dobratz.

The heat of vaporization at 1 atm. (56.5°) found from the determinations of set II is 119.5 cal./g., 6940 cal./mole. This value is lower than that tabulated in the "International Critical Tables,"[9] which is 124.5 cal./g.

The precision of the calorimetric data and the agreement between the two sets are good at the lower temperatures. The accuracy at 100° and lower is considered to be about 1%, as confirmed by check determinations with benzene.[4] At the higher temperatures the precision of the set I determinations was poorer. The accuracy of the 150° value of set II is probably within 2%.

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(7) Wiedmann, Wied. Ann., 2, 195 (1877).

(8) Regnault, Me. del' Acad., 26, 1 (1862).

(9) "International Critical Tables," Vol. V, McGraw-Hill Book Co., Inc., New York, N. Y., 1929, p. 138.

On Erickson's Melting Point Formula for Straight-Chain Dicarboxylic Acids

BY LEO F. EPSTEIN

Erickson[1] has recently published a curious iterative empirical formula for the centigrade melting point T_n of a straight chain dicarboxylic acid containing $(n + 2)$ carbon atoms, viz.

$$T_n = 100 \, d_n + 80 \tag{1}$$
$$d_n = (0.095)^{0.85} \, d_{n-1} \tag{2}$$

with the initial value $d_2 = 0.873$. By numerical calculation, carried up to $n = 30$, he finds that as n approaches infinity, $d_\infty \to 0.43$ and $T_\infty \to 123°$. This formulation is, so far as is known, the first time that an empirical function has been found which reproduces the odd-even oscillatory nature of the dicarboxylic acid melting points. Other substances[2] (e. g., the fatty acids) also exhibit this peculiar behavior, for melting points and other physical properties (e. g., aqueous solubilities).

This note is intended as a guide in fitting an Erickson-type formula to other data, by pointing out the limitations in the choice of constants, and by showing how the limiting value of the sequence can readily be computed without calculating all the intermediate values.

It follows from (2) that

$$d_n = C^{C^{C^{C^{C^{d_2}}}}} \ldots \ldots (n - 2) C\text{'s} \tag{3}$$

with $C = (0.095)^{0.85} = 0.13523$ in the present case. Then

$$d_\infty = C^{C^{C^{C}}} \cdots \tag{4}$$

with an infinite number of terms, provided that C has a value such that the sequence converges. It is obvious that when $C = 0$, $d_\infty = 0$ and when $C = 1$, $d_\infty = 1$. By inspection, (4) can be written $d_\infty = C^{d_\infty}$. To establish the range of values of C for which a finite limit exists, consider the transcendental equation for d_∞, obtained by taking logarithms in (4)

$$d_\infty = \ln d_\infty / \ln C \tag{5}$$

by writing $y_1 = x$ and $y_2 = \ln x / \ln C$, it will be seen that the sequence converges and $d_\infty = x$ exists when $y_1 = y_2$. Plotted against x, y_1 is a straight line with a unit slope through the origin; and y_2 is minus infinity at the origin, and increases monotonically, crossing the $y = 0$ line when $x = 1$, for all values of C. These two curves will

(1) John G. Erickson, THIS JOURNAL, 71, 307 (1949).

(2) J. F. Norris, "The Principles of Organic Chemistry," 3rd ed., McGraw-Hill, New York, N. Y., 1931, p. 142.

either coincide at one or two points in the positive quadrant or not at all, depending on the value of C. If they do not intersect, the sequence (4) does not converge. The limiting case will occur when the two curves osculate, $i.\ e.$, when $y_1 = y_2$ and $dy_1/dx = dy_2/dx$, where the two roots will coincide. The first of these equations is equivalent to (5), the second is

$$d_\infty \ln C = 1 \qquad (6)$$

Solving (5) and (6) simultaneously for C yields $C = e^{1/e} = 1.4447$. Thus (4) will converge as long as C is less than this value, for which $d_\infty = e$. When $0 < C < 1$, the slope of y_2 is negative, and there will be only one point where the curves intersect. In the region $1 < C < e^{1/e}$, there will be two finite roots; thus, for example, when $C = 1.2$, equation (5) is satisfied by the two values $d_\infty = 1.2577$ and 14.7675. Since physically T_∞ and d_∞ must be uniquely determined, only values of C lying between zero and unity will be suitable for empirical formulas of this type.

The roots of (5) can be found by iteration or any other conventional method for solving transcendental equations. Using the value $C = 0.13523$ chosen by Erickson, $d_\infty = 0.42622$ and $T_\infty = 122.6°$, in excellent agreement with Erickson's result and the available experimental data.

d_∞ is independent of the value of d_2. Other functional relations of the form $x_n = f(x_{n-1})$, with simple restrictions on the nature of $f(x)$, will also give the odd–even oscillatory character of this function, converging to a limit independent of the starting value.

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(3) The Knolls Atomic Power Laboratory is operated by the General Electric Research Laboratory for the Atomic Energy Commission. The work reported here was carried out under contract No. W-31-109 Eng-52.

A New Method for the Preparation of the Thiazole Moiety of Thiamine

BY ALBERT J. EUSEBI, ELLIS V. BROWN AND LEOPOLD R. CERECEDO

In a previous paper, Cerecedo and Tolpin[1] reported the synthesis of ethyl 4-methylthiazole-5-acetate by condensation of ethyl α-bromolevulinate with thioformamide. Their attempts to reduce this compound to the alcohol, 4-methyl-5 - β - hydroxyethylthiazole, were unsuccessful. This reduction has now been smoothly carried out by the use of LiAlH$_4$. The usefulness of this substance as a reducing agent has recently been established with a variety of organic compounds.[2]

Experimental[3]

To a solution of 2.5 g. (0.066 mole) of LiAlH$_4$ in 100 ml. of anhydrous ether was added a solution of 18.5 g. (0.10

(1) Cerecedo and Tolpin, THIS JOURNAL, 59, 1660 (1937).
(2) Nystrom and Brown, ibid., 69, 1197, 2548 (1947).
(3) Analyses by Dr. F. A. Bühler.

mole) of ethyl 4-methylthiazole-5-acetate in 150 ml. of anhydrous ether at a rate to produce mild reflux of the ether. The reaction was allowed to continue for fifteen minutes after the last addition. The mixture was then cooled, and water added dropwise to decompose the excess of LiAlH$_4$. The precipitate was treated with an excess of alkali, and the mixture extracted with three 100-ml. portions of ether. The combined ether extracts were dried with sodium sulfate, and the ether removed in $vacuo$. The light brown residue was distilled under diminished pressure at 91–95° (2 mm.). The yield was 7 g. (49%). In a second run with smaller quantities of reactants a 62% yield was obtained.

Picrate of 4-methyl-5-β-hydroxyethylthiazole (I), after recrystallization from ethanol, melted at 162° (uncor.).

$Anal.$ Calcd. for $C_{12}H_{12}O_8N_4S$: C, 38.71; H, 3.22; N, 15.05; S, 8.60. Found: C, 39.05; H, 3.06; N, 14.95; S, 8.30.

Picrolonate of (I), recrystallized from ethanol, m. p. 183–185° (uncor.).

$Anal.$ Calcd. for $C_{16}H_{17}O_6N_5S$: C, 47.17; H, 4.18; N, 17.19; S, 7.86. Found: C, 47.10; H, 4.18; N, 16.94; S, 7.84.

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Preparation of 3-Ethylpyridine

BY T. I. FAND AND C. F. LUTOMSKI

The preparation of 3-ethylpyridine from 3-acetylpyridine using the general method of Wolff–Kishner has been reported by Woodward,[1] but the yield of pure product is not given. The need for rather large quantities of 3-ethylpyridine prompted a search for conditions giving a better yield. The method finally adopted which gave an 80% yield of 3-ethylpyridine from 3-acetylpyridine was the Huang-Minlon[2] modification of the Wolff–Kishner reaction. The amount of triethylene glycol used by Huang-Minlon[2] could be reduced to one-third without diminution of yield.

Procedure

One liter of triethylene glycol (Carbide and Carbon Chemicals Corp.), 242 g. of 3-acetylpyridine, 270 g. of 85% hydrazine hydrate (Edwal Labs.), and 225 g. of potassium hydroxide pellets were heated in a 2-liter flask equipped with a stirrer and reflux condenser for one hour by means of an oil-bath maintained between 110–125°. The reflux condenser was then changed for distillation and the temperature of the oil-bath was raised over a period of one-half hour to 185–190° and maintained there for two hours, during which period the product distilled over. The distillate was extracted with ether, dried over potassium carbonate and finally fractionated through a 3-ball Snyder column. A main fraction was collected boiling between 165.5–166° at atmospheric pressure. The yield was 172 g. or 80%. The picrate melted at 129–130°. The boiling point of 3-ethylpyridine is reported[3] as 165–165.3°, and the melting point of the picrate is reported[4] as 128–130°.

NEPERA CHEMICAL CO., INC.
YONKERS 2, N. Y.   RECEIVED APRIL 13, 1949

(1) C. F. Woodward, A. Eisner and P. G. Haines, THIS JOURNAL, 66, 911 (1944).
(2) Huang-Minlon, ibid., 68, 2487 (1946).
(3) Stoehr, J. prakt. Chem., [2] 45, 35 (1892).
(4) Stoehr, ibid., [2] 45, 33 (1892).