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The Heats of Solution of Hexamethylbenzene, Cetyl Alcohol, and Dicetyl in Related Liquids; Heats of Fusion by an Extrapolation Process

GEORGE S. PARKS AND ROBERT D. ROWE

Department of Chemistry, Stanford University, Stanford University, California

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The heats of solution of crystalline hexamethylbenzene, cetyl alcohol, and dicetyl in various related liquids have been obtained at 25°C. Benzene, toluene, xylene, and mesitylene have been used as solvents for hexamethylbenzene, and a value for the heat of fusion of this substance has been deduced from these heats of solution by an extrapolation process. Similarly, a series of alcohols (methyl, ethyl, *n*-butyl, *n*-heptyl, and *n*-dodecyl) have been used for the solution of cetyl alcohol. Solubility limitations, however, made it impractical to employ any liquid paraffin except *n*-heptane in the case of dicetyl. The heats of fusion at 25°C, as estimated from the present solution experiments, are per gram: hexamethylbenzene, 29.0 ± 0.3 cal.; cetyl alcohol, 48.2 ± 0.7 cal.; and dicetyl (dotriacontane), 58.7 ± 1.2 cal.

INTRODUCTION

THE heat of solution of a crystalline substance in a liquid with which it forms an ideal or "perfect" solution is theoretically its heat of fusion at the temperature of the solution process.¹ Accordingly, the calorimeter which the authors² previously developed for measuring the heats of solution of various forms of glucose in water has now been used to measure the heats of solution of hexamethylbenzene, cetyl alcohol, and dicetyl (dotriacontane) in some related liquids at about 25°C, and particularly in the case of the first two substances to obtain a fairly accurate value for the heat of fusion at this temperature by an extrapolation process. Fusion data of this sort can then be combined with the heats of combustion, entropies, and free energies of the crystalline substances so as to yield corre-

sponding values at 25° for the hypothetical liquid state. Such a procedure is frequently advantageous, since regularities are more pronounced in any homologous series, or related group, of organic compounds if the comparisons are based upon the liquid state rather than upon the more individualistic crystalline forms.

APPARATUS AND METHOD

The essential features of the calorimetric assembly have been described in our previous paper.²

The experimental procedure involved the dissolving of suitable amounts of the crystalline solute (hexamethylbenzene, cetyl alcohol, or dicetyl, as the case might be) in 250 ml portions of related liquids. The initial temperature of these liquids was around 25°, and the amount of crystalline solute employed generally gave a subsequent temperature lowering of about two degrees. The various values for the heats of

¹ J. H. Hildebrand, *Solubility* (Reinhold Publishing Corporation, New York, 1936), second edition, p. 57.

² R. D. Rowe and G. S. Parks, *J. Chem. Phys.* **14**, 383 (1946).

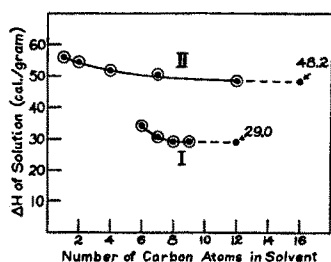


FIG. 1. Graph I shows the mean results for the heats of solution of crystalline hexamethylbenzene in benzene, toluene, xylene, and mesitylene with an extrapolation to a hypothetical value of 29.0 cal./g for the fusion process at 25°C. Likewise, Graph II shows the heats of solution of crystalline cetyl alcohol in a series of normal aliphatic alcohols with an extrapolation to a value of 48.2 cal./g for the fusion process.

solution thus obtained were then adjusted to the reference temperature of 25° by use of Kirchhoff's law with a suitable value for ΔC_p , the difference between the heat capacity of the dissolved and crystalline solute.

The most desirable application of this solution procedure to obtain a value of the heat of fusion of the crystalline solute involves the employment of a series of liquid solvents which approach progressively the chemical formula of the solute. With the aid of the corresponding data for the heats of solution, an extrapolation process to the solute itself can thus yield an accurate value for the heat of fusion. In the present measurements this method gave fairly satisfactory results both for hexamethylbenzene and for cetyl alcohol. However, the very limited solubility³ of dicetyl in paraffinic hydrocarbons above *n*-heptane rendered such an extrapolation impractical with this particular substance.

SOLUTION DATA FOR HEXAMETHYLBENZENE

The heats of solution of hexamethylbenzene were measured in a series of experiments with benzene, toluene, *m*-xylene, and mesitylene as solvents. The resulting solutions were in all cases 0.287 (± 0.003) molal. In this work Eastman's crystalline hexamethylbenzene was used without further purification and the four solvents were high grade C.P. materials. The necessary data for the heat capacities of crystalline and liquid hexamethylbenzene and for liquid benzene, xylene, and mesitylene were derived from the

³ W. F. Seyer, J. Am. Chem. Soc. **60**, 827 (1938).

previous investigations of Parks and co-workers⁴; likewise, specific heat values for liquid toluene were deduced from the calorimetric studies of Kelley⁵ and of Vold.⁶ The various heats of solution were finally adjusted to the standard temperature of 25°C by the assumption of 0.035 calorie per gram per degree for the temperature coefficient of these solution processes.

The enthalpy data so obtained are summarized in Table I and the mean values are also represented graphically in Fig. 1. The values found with xylene and mesitylene as solvents indicate that these heats of solution are rapidly approaching a limiting value as additional methyl groups are introduced into the benzene ring. Accordingly, from our plot we have taken 29.0 ± 0.3 calories as the heat of fusion for a gram of hexamethylbenzene at 25°.

By use of Kirchhoff's law with a value of $\Delta C_p = 0.035$, deduced from the heat capacity data of Spaght, Thomas, and Parks,⁴ we have also computed a value of 33.9 ± 0.8 calories per gram for the heat of fusion of hexamethylbenzene at 165.5°C, the normal melting point. Actually Spaght, Thomas, and Parks, by means of their radiation calorimeter, found a heat of fusion of 30.4 cal. per g at the melting point together with a heat of transition of 2.6 cal. per g at 110°C, or thus a total transition-fusion effect of about 33.0 ± 0.8 cal. per g.

SOLUTION DATA FOR CETYL ALCOHOL

The heats of solution of cetyl alcohol were also measured in a series of experiments with methyl, ethyl, *n*-butyl, *n*-heptyl, and *n*-dodecyl alcohols

TABLE I. Heats of solution of crystalline hexamethylbenzene in related liquids at 25°C.

Experiment No.	ΔH_{298} of solution (calories per gram) in			
	Benzene	Toluene	Xylene	Mesitylene
1	34.23	30.89	29.14	29.14
2	34.17	30.64	28.86*	29.20
3	—	—	29.22	—
Mean result	34.20	30.76	29.18	29.17

* This value was omitted in deriving the mean result.

⁴ M. E. Spaght, S. B. Thomas, and G. S. Parks, J. Phys. Chem. **36**, 882 (1932); H. M. Huffman, G. S. Parks, and A. C. Daniels, J. Am. Chem. Soc. **52**, 1547 (1930); H. M. Huffman, G. S. Parks, and M. Barmore, *ibid.* **53**, 3876 (1931).

⁵ K. K. Kelley, J. Am. Chem. Soc. **51**, 2738 (1929).

⁶ R. D. Vold, *ibid.* **59**, 1515 (1937).

as solvents. Here the resulting solutions were 0.130 (± 0.005) molal except in the first experiment with ethyl alcohol, where a 0.210-molal solution was the product. In this work Eastman's cetyl alcohol (m.p. 48–49°) was used without further purification, as previous investigations in this Laboratory had demonstrated that its purity was quite adequate for the present purpose. The first four alcohol solvents were C.P. materials which were further purified by dehydration over quicklime and fractional distillation. The sample of dodecyl alcohol, which had been prepared in this laboratory by Dr. Martin E. Synerholm, was estimated to contain about 90 percent of the normal alcohol with 10 percent of related alcohols. It boiled at 150°–155° at a pressure of 21 mm; its melting point was 17.3°C; and it had a density of 0.8290 at 25°.

The necessary data for the heat capacity of crystalline cetyl alcohol and the first four solvent liquids were obtained from previous studies⁷ which had been carried out in our Stanford Laboratory. The specific heat of the liquid dodecyl alcohol was estimated by extrapolation of the data for these lower alcohols.

The various experimental heats of solution were adjusted to 25°C by assuming 0.13 calorie per gram per degree for the temperature coefficient of these solution processes. The enthalpy data so obtained are summarized in Table II and are represented graphically in Fig. 1. Of the several sets of results, those with the dodecyl alcohol are unfortunately the least reliable, partly because of the impurities in this particular preparation and the estimate of its specific heat by extrapolation and partly because the cetyl alcohol samples tended to float on the surface of the solvent liquid and required at least two minutes for the solution process even though the rate of stirring was increased from 505 to 650 r.p.m. In view of these elements of uncertainty only moderate weight was given to the results with dodecyl alcohol in extrapolating the curve in Fig. 1 to yield an ideal value of 48.2 cal. per g for the heat of solution of crystalline cetyl alcohol in a hypothetical liquid cetyl alcohol at

TABLE II. Heats of solution of crystalline cetyl alcohol in related liquids at 25°C.

Experiment No.	Methyl alcohol	ΔH_{298} of solution of Ethyl alcohol	(calories per gram) in n -Butyl alcohol	n -Heptyl alcohol	n -Dodecyl alcohol
1	56.38	54.33	52.27	51.01	48.96
2	55.52	54.28	51.77	50.82	48.12
3	—	54.45	51.12	50.28	48.30
4	—	54.42	51.65	50.19	—
5	—	54.05	—	50.27	—
Mean	55.95	54.30	51.70	50.51	48.46

25°C. This value, therefore, represents the heat of fusion at 25°.

By Kirchhoff's law with the assumption of $\Delta C_p = 0.13$ cal. per g for the fusion process, we also computed initially a value of 51.3 cal. per g for the heat of fusion at 49.3°, the normal melting point of cetyl alcohol crystals.^{8a} This fusion estimate is considerably larger than the experimental result of Tammann, 33.8 cal. per g, which is quoted by the *International Critical Tables*^{8b} and the very early result of 29.2 cal. per g obtained by Favre and Silbermann.⁹ At first we were at a loss to explain such a great discrepancy, especially as our higher value fitted in well with entropy data for the series of normal aliphatic alcohols in the liquid state. Later Baker and Smyth,¹⁰ however, pointed out that crystalline cetyl alcohol undergoes an important transition at 32–35°C; and from a time-temperature heating curve, made in our laboratory by Dr. George E. Moore, we now estimate that this heat of transition amounts to about 47 percent of the actual heat of fusion. Accordingly, when we divide our preceding fusion estimate for 49.3°, which was computed without reference to such a transition, by the factor 1.47, we thus obtain a revised fusion value of 34.9 cal. per g together with a heat of transition of 16.4 cal. per g. In view of such results, nevertheless, it still seems probable that these earlier experimental determinations of the heat of fusion are somewhat low, perhaps because of an inadequate allowance for premelting.

⁸ *International Critical Tables*, (a) Vol. I, p. 260; (b) Vol. V, p. 134.

⁹ Quoted in the Landolt-Bornstein-Roth Scheel *Tabellen* (Verlagsbuchhandlung Julius Springer, Berlin, 1923), p. 1472.

¹⁰ W. O. Baker and C. P. Smyth, *J. Am. Chem. Soc.* **60**, 1229 (1938).

⁷ G. S. Parks, *J. Am. Chem. Soc.* **47**, 338 (1925); and an unpublished investigation by G. S. Parks, W. D. Kennedy, and G. E. Moore, dealing with n -heptyl and cetyl alcohols.

TABLE III. Heat of solution of crystalline dicetyl in *n*-heptane at 25°C.

Experiment No.	Grade of solvent	ΔH_{298} of solution (in calories per gram)
1	"Practical"	58.5
2	"Practical"	56.6
3	"Practical"	59.1
4	"Practical"	60.0
5	"Practical"	60.3
6	"Highest purity"	57.6
7	"Highest purity"	58.7
Final mean value		58.7(± 0.9)

SOLUTION DATA FOR DICETYL

Our original plan had been to measure the heats of solution of samples of crystalline dicetyl (dotriacontane) in several liquid normal paraffins, including the heptane, decane, and hexadecane. However, it was soon found that the limited solubility and slow rate of solution of the crystals in these two latter solvents at 25° rendered such a procedure experimentally impractical. Thus our present results pertain only to the formation of 0.030 molal solution with *n*-heptane as solvent. Even these are considerably less consistent than our previous results with hexamethylbenzene and cetyl alcohol, partly because the present solubility limitations made it necessary to use dicetyl samples which gave a temperature lowering of only about one degree and partly because the time of solution, in this case several minutes, necessitated larger and more uncertain corrections for heat exchange between the calorimeter and its jacket.

The dicetyl and the *n*-heptane used herein were Eastman materials. The former melted at 68–69.5°. Two grades of solvent, "practical" and "highest purity," were employed without significant differences in the enthalpy values, although the solution process took place somewhat more readily in the "practical" material. The necessary data for the heat capacities of crystalline dicetyl and liquid *n*-heptane were derived from previous investigations of Parks and co-workers.¹¹

¹¹ G. S. Parks, H. M. Huffman, and S. B. Thomas, J. Am. Chem. Soc. **52**, 1032 (1930); and an unpublished study on dicetyl by G. S. Parks and J. A. Hatton.

The results of seven determinations of the heat of solution are reported in Table III. The final mean of 58.7 cal. per g involves an average deviation of ± 0.9 cal. Under the circumstances we now suggest this mean result as the best value for the heat of fusion of dicetyl at 25°, with an over-all uncertainty of perhaps 1.2 cal. when some allowance is made for departures from ideality in the dicetyl-heptane solution. From the solubility studies of Seyer,³ we have also computed a value of 59.0 cal. per g for the ideal heat of solution at 40°. With the plausible assumption¹¹ of 0.06 cal. per g for the temperature coefficient of the solution process, this value yields 58.1 cal. at 25°, which is in reasonable agreement with our present mean result.

By use of Kirchhoff's law with the assumption of $\Delta C_p = 0.06$ cal. per g for the fusion process, we now estimate from our mean result a value of 61.4 cal. per g for the heat of fusion of dicetyl at 70.2°C, the normal melting point.³ The literature apparently contains no experimental value for the heat of fusion of this hydrocarbon, but Garner, Van Bibber, and King¹² have reported the following heats of fusion per gram for two closely related paraffins at their respective melting points:

<i>n</i> -C ₃₀ H ₆₂	59.6 cal. per g,
<i>n</i> -C ₃₄ H ₇₀	63.9 cal. per g.

The mean of these, 61.8 cal. per g, is thus in very good agreement with our present computed value for *n*-C₃₂H₆₆. Of course, it should be noted here that such fusion values really include the heat of transition for the α – β transformation of the crystalline hydrocarbon, which takes place a few degrees below the normal melting point.

ACKNOWLEDGMENT

Before concluding, the authors wish to acknowledge their indebtedness to Mr. John A. Hatton, who made the measurements of the heats of solution of dicetyl in *n*-heptane for this study.

¹² W. E. Garner, K. Van Bibber, and A. M. King, J. Chem. Soc. **1931**, 1533.