

505. *The Solubility of Benzene in Water.*

By F. FRANKS, M. GENT, and (in part) H. H. JOHNSON.

The solubility of benzene in water has been measured over the temperature range 17—63° by ultraviolet absorptiometry. The results are in very good agreement with those of Arnold *et al.*¹ and the two sets of observations have been combined for the purposes of a statistical analysis. It is shown that the usual interpolation equation $\ln x_2 = -A/T + B \ln T + C$ is incapable of representing the experimental data which can best be expressed by a fifth-degree polynomial. The thermodynamic functions of solution have been computed, and it is found that ΔC_p shows a maximum and a minimum at 25° and 48°, respectively. The results are interpreted in terms of a structural transition in liquid water caused by the partial collapse of a structure of gas-hydrate type to a more closely packed one as the temperature is raised. The evidence for such a transition is briefly reviewed.

THE heat-capacity change, ΔC_p , associated with dissolution is likely to provide useful information on the structure-promoting or structure-breaking influence of solutes on water. However, the calculation of heat capacities from solubility data requires very accurate experimental determinations. A recent review² of the more reliable measurements of the solubilities of inert gases shows a considerable scatter in the experimental results. Therefore, for the present study benzene was chosen as solute, because, whilst

¹ Arnold, Plank, Erickson, and Pike, *Ind. Eng. Chem., Chem. Eng. Data Ser.*, 1958, **3**, 253.

² Himmelblau, *J. Phys. Chem.*, 1959, **63**, 1803.

it does not dissociate or combine chemically with water, it can be accurately estimated even at very low concentrations.

The solubility of benzene in water has been the subject of many studies,^{1,3,4} but the agreement between them is rather poor. Accordingly the present investigation was undertaken to provide more experimental results, and it was hoped that by combining the results with one of the published sets a reliable expression might be obtained for the solubility as a function of temperature which would be of sufficient accuracy for the computation of ΔC_p values. We believe this to have been achieved.

EXPERIMENTAL

Methods of Measurement.—To overcome the evaporation of benzene during the handling of its aqueous solutions, the dilution technique common to earlier work was discarded. The optical densities of saturated solutions were measured directly at 254 m μ on a Unicam S.P.

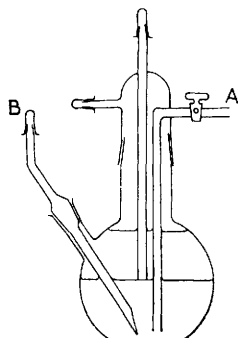


FIG. 1. Equilibration flask.

500 spectrophotometer fitted with a thermostat-controlled cell-holder capable of maintaining the temperature within $\pm 0.05^\circ$. Two independent methods were used in carrying out the solubility determinations:

(i) Water and benzene were placed in the equilibration flask (Fig. 1) which was then suspended in a water-thermostat bath. Purified nitrogen was blown through the liquid phases for 24 hr. The nitrogen flow was then stopped and the flask left in the thermostat-bath for a further 24 hr. to allow the liquid layers to separate completely. Nitrogen pressure was then applied at A, and the aqueous phase was forced out at B into a tared optical cell which was immediately stoppered and weighed. The optical path length was chosen so that the optical densities measured always lay between 0.30 and 0.55. The cell was then inserted into the cell-holder, and the optical density of the solution was determined after 1 hr. Reproducible results were obtained only by using polytetrafluoroethylene stoppers in the cells, since considerable evaporation occurred through ground quartz joints. Samples were taken on consecutive days, and the constancy of the optical density at a given temperature indicated that the solution was saturated with respect to benzene.

(ii) 0.3 ml. of water was placed in a 0.1 cm. stoppered optical cell and 0.05 ml. of benzene added. The cell was placed in the cell-holder and left until a constant optical density was obtained (~ 20 hr.). The temperature was then raised by a few degrees and the procedure repeated. After the highest temperature had been reached (63°), the solution was allowed to cool, several more optical densities being determined.

The two methods gave identical results within experimental error ($\pm 0.5\%$ in the optical-density measurement).

Calibration.—Standard solutions of benzene in degassed water covering the concentration range 0.01–0.2% by weight of benzene were prepared at 60° by the method described by Arnold *et al.*¹ Samples were transferred to the optical cells by nitrogen pressure, and the cells were immediately stoppered. The optical density of each of 15 standard solutions was measured at 60° . The optical densities of the solutions whose concentrations lay below 0.1% by weight

³ Bohon and Claussen, *J. Amer. Chem. Soc.*, 1951, **73**, 1571.

⁴ Alexander, *J. Phys. Chem.*, 1959, **63**, 1021.

of benzene were also determined at 50°, 40°, 30°, and 20°. The calibration experiments confirmed the findings of Arnold *et al.* that aqueous solutions of benzene do not obey Beer's law. A least-squares analysis indicated that the optical densities (O.D.) could be represented in terms of the concentration in % by weight of benzene (w) by the expression

$$\text{O.D.} = 20.3911w - 32.7930w^2,$$

which is in good agreement with published results.¹

No significant change in the optical density could be detected as the temperature of the samples was reduced from 60° to 20°. This again confirms the findings of Arnold *et al.* who measured optical densities in the temperature range 3—25°.

Materials.—Thiophen-free benzene was recrystallized twice from ethanol, washed, filtered through silica gel, and distilled.⁵ Deionized water was doubly distilled from alkaline potassium permanganate and aqueous phosphoric acid. It was collected and stored under purified nitrogen. As criteria of purity the specific conductance (1×10^{-7} ohm⁻¹ cm.⁻¹) and the surface tension (71.9 dyne cm.⁻¹ at 25°) were chosen.⁶

Results.—The experimental results are shown in the first two columns of Table 1. Concentrations of benzene in saturated solutions at $T^\circ\text{K}$ are expressed in mole fractions x_2 . The

TABLE 1.

Solubilities of benzene (results of Arnold *et al.*¹ are indicated by †).

$T^\circ\text{K}$	10^4x_2	$10^3/T$	$\ln(f_2/x_2)$	$T^\circ\text{K}$	10^4x_2	$10^3/T$	$\ln(f_2/x_2)$	$T^\circ\text{K}$	10^4x_2	$10^3/T$	$\ln(f_2/x_2)$
278.2°	4.02 †	3.595	11.391	300.5°	4.02 †	3.328	12.489	319.2°	4.57	3.133	13.143
279.9	4.02 †	3.573	11.481	302.2	4.02	3.309	12.565	323.0	4.71 †	3.096	13.258
282.2	3.99 †	3.544	11.607	303.2	4.09 †	3.298	12.593	324.2	4.78	3.058	13.291
285.7	3.97 †	3.500	11.794	305.2	4.12	3.277	12.674	327.7	4.96 †	3.502	13.380
288.2	3.99 †	3.470	11.914	308.2	4.20	3.245	12.782	329.2	5.03	3.038	13.422
290.2	3.95	3.466	12.024	313.1	4.34 †	3.194	12.952	333.0	5.22 †	3.003	13.523
293.2	3.95 †	3.411	12.169	313.7	4.39	3.188	12.966	334.2	5.31	2.992	13.546
295.2	3.97	3.388	12.257	315.2	4.40	3.173	13.026	336.2	5.42	2.974	13.597
298.0	3.95 †	3.356	12.393	317.2	4.45	3.153	13.081	338.0	5.56 †	2.959	13.631
298.1	4.02 †	3.355	12.379	318.2	4.55 †	3.143	13.109	342.4	6.00 †	2.921	13.703
299.2	3.99	3.342	12.436								

results of Arnold *et al.* are included in the Table, since a preliminary comparison indicated that the two sets of results were consistent. This was later confirmed by a formal analysis.

DISCUSSION

The solubility minimum near 18° is characteristic of mononuclear aromatic hydrocarbons and implies that the partial molar heat of solution, ΔH , passes through zero. This has been interpreted by invoking two contributions towards ΔH : a positive heat of cavitation and a negative contribution due to hydrophobic hydration⁷ and/or of complex-formation of a type involving the labile electrons. However, solubility minima have also been observed for the lower paraffins (near 76°) where specific solvent-solute interactions can be excluded.

The computation of ΔH from a $\ln x_2-1/T$ graph implies the choice of the pure liquid hydrocarbon as standard state. This choice has been criticized⁸ on the basis that aromatic hydrocarbons possess some structure of their own, and the magnetic nature of the association of liquid benzene has recently been discussed.⁹ Using as standard state the hydrocarbon vapour at a pressure of 1 mm., Herington⁸ has calculated the free energy of evaporation of aromatic hydrocarbons from aqueous solution. He found that, for each hydrocarbon, ΔG was a linear function of the temperature, implying that ΔH and ΔS are

⁵ Mair, Termini, Willingham, and Rossini, *J. Res. Nat. Bur. Stand.*, 1946, **37**, 229.

⁶ Franks, *Chem. and Ind.*, 1961, **80**, 204.

⁷ Frank and Evans, *J. Chem. Phys.*, 1945, **13**, 507.

⁸ Herington, *J. Amer. Chem. Soc.*, 1951, **73**, 5883.

⁹ Cheshko, *Zhur. fiz. Khim.*, 1957, **31**, 2260.

constant and ΔC_p is zero. Alexander,⁴ using as standard state benzene vapour at unit fugacity ($f_2 = 1$ mm.), obtained the expression

$$\Delta G = 29,389 - 541.273T + 169.000 \log T,$$

giving rise to

$$\Delta C_p = 73 \pm 5 \text{ cal. deg.}^{-1} \text{ mole}^{-1}.$$

We recalculated our results using the same standard state. Fugacities were calculated by using published data of the second virial coefficient of benzene.¹⁰ Values of $\ln(f_2/x_2)$ at the corresponding reciprocal temperatures are included in Table 1.*

Analysis of Results.—The dependence of solubility on temperature can be expressed in terms of the equation

$$-\Delta H = RT^2 \left(\frac{d \ln(f_2/x_2)}{dT} \right). \quad (1)$$

In order to fit experimental results to an integrated form of eqn. (1), ΔH must be expressed as a function of temperature. An interpolation equation which has been frequently used for this purpose is

$$\ln(f_2/x_2) = -(A/T) + B \ln T + C, \quad (2)$$

giving in turn $-\Delta H = AR + BRT$ and $\Delta C_p = BR$.^{4,11-13} Although eqn. (2) does not accurately express gas solubilities over an extended temperature range, it has been suggested that over a limited temperature interval this equation might provide a sufficiently good fit for the experimental data. Eqn. (2) was therefore fitted to the data in Table 1 by the method of least squares, but the deviations indicated by their non-random appearance that this equation is not satisfactory. A series of polynomials was then fitted to the data, as well as the following equation:

$$\ln(f_2/x_2) = AT^{-1} + B + C \ln T + DT + ET^2 + FT^3, \quad (3)$$

which was included to ascertain whether terms in T^{-1} and $\ln T$ contributed significantly to the goodness of the fit, and hence to ΔH . It was found that a fifth-degree polynomial provided the best fit, *i.e.*, a sixth-degree polynomial was not significantly better. Eqn. (3) did not provide as good a fit as the fifth-degree polynomial. A measure of the goodness of fit of the above equations is obtained by the residual-mean-square (RMS) deviations which are given in Table 2. There is a significant reduction in the RMS deviation on

TABLE 2.
Mean-square deviations of different interpolation equations.

Degree of fitted polynomial.....	4	5	6
Mean square deviation $\times 10^6$	42.3	19.7	20.3

going from a fourth- to a fifth-degree polynomial, but no further reduction is obtained by fitting a higher-degree polynomial. The RMS deviation of 20×10^{-6} is consistent with the known experimental error of $\pm 0.5\%$ in x_2 . When the coefficients are evaluated, the experimental data are expressed as

$$\begin{aligned} \ln(f_2/x_2) &= 8148.8578 - 13,271.443 \times 10^{-2}T + 8628.1641 \times 10^{-4}T^2 \\ &- 2797.2295 \times 10^{-6}T^3 + 452.50417 \times 10^{-8}T^4 - 29.231189 \times 10^{-10}T^5. \end{aligned} \quad (4)$$

* In calculating f_2 , we allowed for the changing mole fraction of benzene in the benzene-rich layer. The necessary data were obtained from determinations of the solubility of water in benzene which were carried out at the same time as the work described above. The results of this study will be reported later.

¹⁰ Francis, McGlashan, Hamann, and McManamey, *J. Chem. Phys.*, 1952, **20**, 1341.

¹¹ Valentiner, *Z. Phys.*, 1927, **42**, 253.

¹² Glew and Moelwyn-Hughes, *Discuss. Faraday Soc.*, 1953, **15**, 150.

¹³ Morrison and Johnstone, *J.*, 1954, **3441**.

Since the experimental determinations of Arnold *et al.*¹ cover a wider temperature range (5–69°) than do our own, individual polynomials were fitted to the two sets of data, in order to check their consistency. The following equations were obtained:

(a) Arnold *et al.*

$$\ln (f_2/x_2) = 12.4672 + 4.1594\theta - 4.075\theta^2 + 2.110\theta^3 + 13.990\theta^4 - 29.780\theta^5; \quad (5)$$

(b) Our data:

$$\ln (f_2/x_2) = 12.4684 + 4.1683\theta - 4.097\theta^2 + 2.014\theta^3 + 14.040\theta^4 - 29.230\theta^5; \quad (6)$$

where $\theta = (T - 300)/100$.

The good agreement between the coefficients of eqns. (5) and (6) indicates that combination of the two sets of data does not appreciably alter the coefficients of the interpolation equation, and that therefore the two sets of data are consistent. This conclusion was verified more formally from a consideration of the RMS deviations.

Thermodynamic Functions of Dissolution.—The thermodynamic functions associated with the transfer of 1 mole of benzene from the ideal gas state ($f_2 = 1$ mm.) to an aqueous solution were obtained from eqn. (4) in the form

$$\Delta G, \Delta H, \Delta S, \Delta C_p = A + BT + CT^2 + DT^3 + ET^4 + FT^5 + GT^6. \quad (7)$$

The polynomial coefficients are given in Table 3, and the thermodynamic functions are shown graphically in Figs. 2 and 3. Since the choice of a particular interpolation equation imposes the shapes of these curves, the thermodynamic functions were also obtained by

TABLE 3.

	ΔG	Polynomial coefficients in eqn. (7).		ΔC_p
		ΔS	ΔH	
A		-16,191.780		
B	+16,191.780	+52,740.714 $\times 10^{-2}$		+52,740.714 $\times 10^{-2}$
C	-26,370.357 $\times 10^{-2}$	-5143.2486 $\times 10^{-3}$	+26,370.357 $\times 10^{-2}$	-10,286.497 $\times 10^{-3}$
D	+1714.4162 $\times 10^{-3}$	+22,232.380 $\times 10^{-6}$	-3428.8324 $\times 10^{-3}$	+66,697.140 $\times 10^{-6}$
E	-5558.0950 $\times 10^{-6}$	-4495.6290 $\times 10^{-8}$	+16,674.285 $\times 10^{-6}$	-17,982.516 $\times 10^{-8}$
F	+899.12579 $\times 10^{-8}$	+348.49424 $\times 10^{-10}$	-3596.5032 $\times 10^{-8}$	+1742.4712 $\times 10^{-10}$
G	-58.082373 $\times 10^{-10}$		+290.41187 $\times 10^{-10}$	

a large-scale graphical interpolation. The results are included in Fig. 3, showing that good agreement is obtained with ΔC_p as expressed by eqn. (7). It has thus been clearly established that ΔC_p is neither zero nor constant over the range of temperature studied, and further that the good agreement between eqns. (5) and (6) suggests that the representation of ΔC_p as a function of temperature as shown in Fig. 3 is of fair accuracy.

Interpretation of Solubility Data.—The elucidation of solute–water interactions is frequently based on the “free volume” concept of entropy,⁷ whereby the solute molecule exerts a structure-promoting influence on water, and the abnormally high values of $-\Delta S$ are ascribed to the restriction of the rotational degrees of freedom of the water molecules in the co-ordination shell. This restriction is a function of the hydrogen bonds of the water molecules¹⁴ and might therefore be expected to depend on the size and shape of the solute molecules. This can be demonstrated in a striking manner by reference to Fig. 4 which shows the solubilities at 25° of a number of benzene derivatives as a function of their van der Waals diameters, derived from experimental or calculated critical data. There is a clear indication of a relation between ΔG of solution and the diameter of the solute molecule.

Beyond doubt the structure of water is the most important single factor in the interpretation of solubility relations. The crystallographic elucidation of the structure of gas hydrates¹⁵ has led to new ideas regarding liquid water, which is now treated as such a hydrate

¹⁴ Pople, *Proc. Roy. Soc.*, 1951, A, 205, 163.

¹⁵ von Stackelberg and Mueller, *Z. Elektrochem.*, 1954, 88, 25.

consisting of hydrogen-bonded frameworks stabilized by "monomeric" H_2O molecules.¹⁶ Adopting a specific model based on the structure of chlorine hydrate, Frank and Quist have been able to derive expressions for the thermodynamic properties of liquid water and aqueous solutions.¹⁷ This model has been further refined¹⁸ and a dual-structure model has recently been proposed which consists of an equilibrium between the ice-lattice structure and a denser structure in which water molecules occupy the cavities.¹⁹ On the

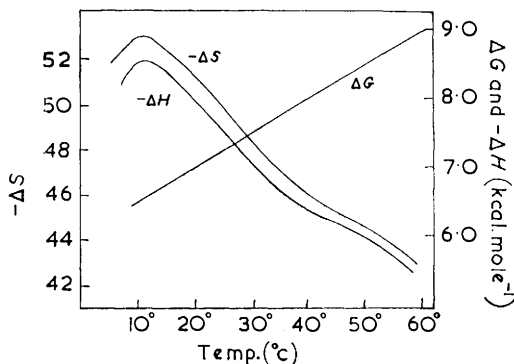


FIG. 2.

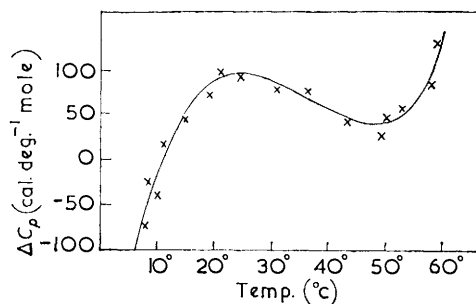


FIG. 3.

FIGS. 2 and 3. Thermodynamic functions.

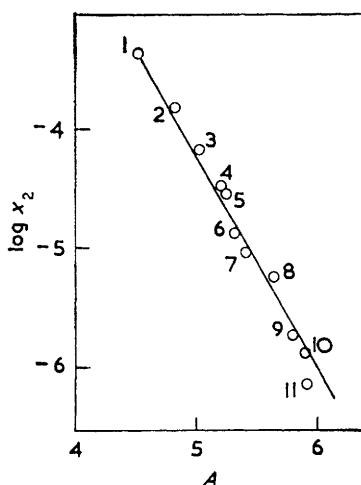


FIG. 4. Solubility of benzene derivatives, $\text{C}_6\text{H}_5\text{X}$, where $\text{X} =$ (1) H, (2) Me, (3) Et, (6) Pr^i , (7) Pr^n , (8) Bu^t , (9) Bu^n , (10) *t*-pentyl, and (11) Ph, and of (4) *m*-xylene and (5) *p*-xylene.

basis of this model the calculated mole fraction of monomeric water at 0° is 0.25, in good agreement with the value of 0.28 obtained from ultrasound absorption in water.²⁰

Although the above models have proved useful in the interpretation of the volumetric properties of water, none of them can satisfactorily explain the reaction of water to non-polar solutes. To reconcile the clathrate-type structural model for liquid water with observed heats and entropies of solution we can postulate that the introduction of a solute molecule into water leads to the formation of different cavities from those which normally

¹⁶ Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N.Y., 1960, p. 472.

¹⁷ Frank and Quist, *J. Chem. Phys.*, 1961, **34**, 604.

¹⁸ Malenkov, *Doklady Akad. Nauk S.S.S.R.*, 1961, **137**, 1354.

¹⁹ Namiot, *Zhur. strukt. Khim.*, 1961, **2**, 476.

²⁰ Hall, *Phys. Rev.*, 1948, **73**, 775.

exist. These involve more water molecules, thus giving rise to an additional contribution to the large, negative entropy of solution, this latter contribution being very sensitive to the size of the solute molecule. In the case of aromatic or unsaturated solutes additional specific interactions are involved, since $-\Delta S$ for such compounds is always greater than for saturated compounds of the same molecular diameter. A model for aqueous solutions of non-polar solutes based on these modifications of the Pauling structural model is now being developed and will be described later.

The abnormal shapes of the ΔH , ΔS , and ΔC_p curves must be explained in terms of the effect of temperature on liquid water. In general, the structure-promoting influence of solutes markedly decreases with rise in temperature, a fact which is shown by the large positive ΔC_p . The main contribution towards these ΔC_p values is provided by the bending of hydrogen bonds in the more ordered structure of the co-ordination shell,²¹ and it has been shown that even above 200° the structural rigidity of co-ordinated water is not destroyed. This observation, however, does not preclude the possibility of one or more structural changes in water; indeed one such transition is provided for in the models discussed:^{17,19} if a fraction α of the molecules is involved in structural units and ν molecules are required to provide one cavity capable of accommodating one monomer or solute molecule, then the limiting conditions for the model are $\alpha = 1$ and $\alpha = [\nu/(\nu + 1)]$. Thus, when more monomer is produced, *e.g.*, by melting of the structure, than can be accommodated, the model breaks down and its place is taken by some other structure, still extensively hydrogen-bonded, but more closely packed than the low-temperature model. Such a transition would be influenced by pressure, temperature, and the presence of solutes. Evidence for such a transition is provided by the change in the shape of the interfacial-tension (water–benzene)²² and viscosity isotherms²³ as functions of pressure. The physical properties of water which indicate a structural transition near 30° have been summarized before;²⁴ further evidence for such a transition is provided by the temperature-dependence of the partial molar volumes of alcohols in aqueous solution,²⁵ and the volumetric behaviour of water–hydrogen peroxide mixtures.²⁶

The thermodynamic functions shown in Figs. 2 and 3 must be interpreted in terms of the different processes involved: (i) the general structure-promoting influence of benzene, giving rise to the large negative ΔS ; (ii) the overall order-depleting effect of temperature on the hydrogen-bonded structure of water, with a positive contribution towards ΔC_p and (iii) the structural transition over a narrow temperature range from a porous to a more closely packed structure which may, however, be more ordered than the low-temperature structure, thus giving rise to the inflexion in the ΔS curve.

Reference to Fig. 2 shows that, although ΔH and ΔS decrease with rise in temperature, the rate of decrease is checked over the temperature range 25–48°. The entropy and enthalpy effects are almost complementary, so that at first glance no striking discontinuity is observed in ΔG , and hence in the solubility polytherm. It is probably this phenomenon, common to many aqueous systems, which was responsible for Herington's findings that ΔG was a linear function of T , implying zero ΔC_p , and that no structure-promoting influence could be ascribed to the solute.⁸ On the basis of the transition suggested, the maximum in the ΔC_p curve corresponds to the onset of a reduction in the freedom of the hydrogen-bond vibrations. With further rise in temperature this restrictive effect is overcome and at 35° the inflexion indicates the balance between the effects of thermal agitation and the restrictions imposed by the structural transition. This type of behaviour should be noticeable in all aqueous systems, provided that no invalid simplifications are

²¹ Claussen and Polglase, *J. Amer. Chem. Soc.*, 1953, **75**, 552.

²² Michaelis and Hauser, *J. Phys. Colloid Chem.*, 1951, **55**, 408.

²³ Bridgman, "The Physics of High Pressures," Bell, London, 1949, p. 346.

²⁴ Feates and Ives, *J.*, 1956, 2798; Franks and Ives, *J.*, 1960, 741.

²⁵ Franks and Johnson, *Trans. Faraday Soc.*, 1962, **58**, 656; Alexander, *J. Chem. and Eng. Data*, 1959, **4**, 252.

²⁶ Giguere, Knop, and Falk, *Canad. J. Chem.*, 1958, **36**, 883.

made in the interpretation of experimental results, *e.g.*, by imposing the restriction of constant ΔH and/or ΔC_p [see eqn. (2)]. Effects qualitatively similar to those described have been observed in the ionization functions of cyanoacetic acid.²⁴

The maxima in $-\Delta H$ and $-\Delta S$, indicative of zero ΔC_p , were at first believed to be spurious, introduced by the method of curve fitting. However, examination of the solubility polytherms of methane and ethane reveals a behaviour exactly analogous to that of benzene, with inflexions at a low temperature and at 35°, clearly indicating a change in the mechanism of dissolution. Supporting evidence is provided by the partial molar volumes of methane and ethane in water which pass through a maximum between 30° and 35°.²⁷

DEPARTMENT OF CHEMICAL TECHNOLOGY,
INSTITUTE OF TECHNOLOGY, BRADFORD, 7.

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²⁷ Masterton, *J. Chem. Phys.*, 1954, **22**, 1830.
