[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE AND THE RESEARCH DEPARTMENT OF PHILLIPS PETROLEUM COMPANY]

Solid Solution Studies. I. Equilibria in the Binary Systems 2,2-Dimethylbutane–2,3-Dimethylbutane and 2,2-Dimethylbutane–Cyclopentane

BY H. L. FINK, M. R. CINES, F. E. FREY AND J. G. ASTON

In the present paper, complete phase diagrams are presented for the binary systems 2,2-dimethylbutane–2,3-dimethylbutane and 2,2-dimethylbutane–cyclopentane. Smittenberg, Hoog and Henkes[1] have studied the solid–liquid equilibria in the binary systems *n*-octane–*n*-nonane and 2,2,3-trimethylbutane–2,2,3,3-tetramethylbutane, which they found to exhibit solid solution. So far as we are aware, these systems are the only ones studied in detail involving hydrocarbon systems at low temperatures which exhibit solid solution. It was partly for this reason that this investigation was made. However, all the components of the system herein discussed exhibit rotation in the solid phase so that the binary systems are of particular interest from the standpoint of the type of solid solutions formed between such components.

Cyclopentane and 2,2-dimethylbutane exhibit two solid phase transitions, while 2,3-dimethylbutane exhibits one. In each case, the material stable below the lower transition will be referred to as the α form, that between the two transitions as the β form, while the solid material stable above the upper transition will be designated as γ.

Experimental

Apparatus and Method.—All measurements contained herein were made in an adiabatic calorimeter of the type described by Southard and Brickwedde,[2] modified to allow filling with liquid and emptying without dismantling and with the capacity reduced to 15 cc. The controls were greatly simplified in keeping with the lowered requirements for precision of the thermal data needed in a study of melting points. This apparatus will be described elsewhere.[3] The various compositions studied were prepared by weighing the major component in a weighing bottle and then adding the minor component and reweighing. The mixture was then poured into the calorimeter in the usual manner. The equilibrium temperature of the calorimeter was observed after measured energy inputs from below the region of interest up to temperatures above its point of complete fusion.

The solidus and liquidus points could be obtained from the data in two ways. The first was to plot the temperature *vs.* the total energy input over the entire range. The solidus temperature is the point on the curve where the curvature changes and the liquidus temperature is the point of intersection of the curve in the two phase region and that for the liquid. Figure 1 shows such a plot for a mixture of 26.5% of 2,3-dimethylbutane and 73.5% 2,2-dimethylbutane with solidus and liquidus points marked. The second was to plot the heat capacity of the material *vs.* temperature treating the data in the two phase region (or regions) as though it were data for a single phase, *i.e.*, all heat added was treated as *sensible* heat. The point on the liquidus curve was the break preceding the heat capacity curve for the liquid while the point on the solidus curve was the break following the heat capacity curve for the solid. Fig. 2 shows this type of plot for the same mixture treated in Fig. 1 with the solidus and liquidus points marked.

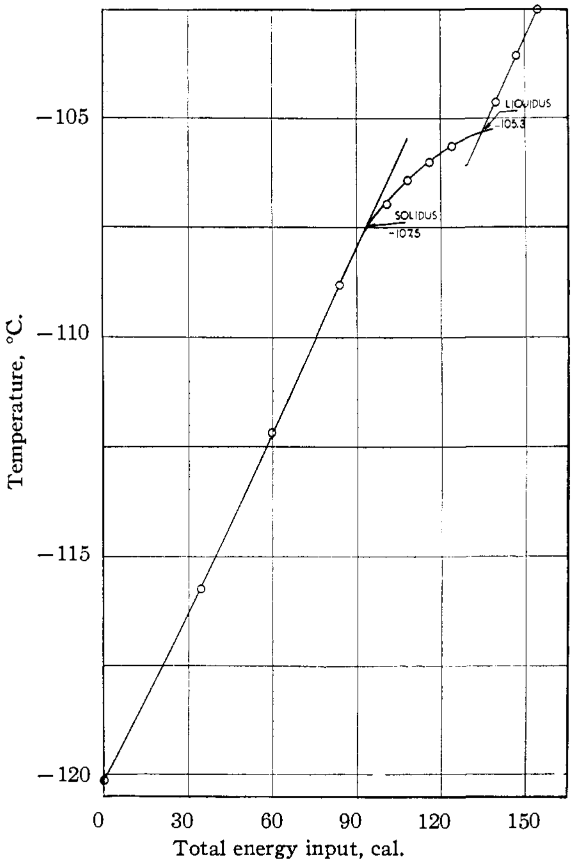

Fig. 1.—Equilibrium temperature *vs.* total energy input plot for 26.5 mole per cent. 2,3-dimethylbutane, 73.5 mole per cent. 2,2-dimethylbutane mixture.

Wherever possible, the value selected for the liquidus point was that read from the graph of energy input *vs.* temperature. It should be noted that this graph is a plot of actual equilibrium temperature *vs.* the total energy added to the calorimeter whereas in the graphs of heat capacity *vs.* temperature, the temperatures are obtained from an average of two equilibrium temperatures. Consequently, the liquidus points obtained from the two curves may differ by as much as 0.5°, the one obtained from the heat capacity graph being higher than the true value. In several cases, the liquidus point was obtained from the heat capacity curve because the break in the energy graph was obscure due to the small heat of fusion. The solidus point in all cases was obtained from the heat capacity plot since the corresponding change in curvature on the energy plot was uncertain by as much as two degrees.

It was possible to calculate approximate heats of transition and fusion by summing the energy inputs during transition and fusion and correcting for the temperature rise.

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[1] Smittenberg, Hoog and Henkes, THIS JOURNAL, **60**, 17 (1938).

[2] Southard and Brickwedde, *ibid.*, **55**, 4378 (1933).

[3] J. G. Aston, H. L. Fink, J. W. Tooke and M. R. Cines, *Ind. Eng. Chem., Anal. Ed.*, **19**, 218 (1947).

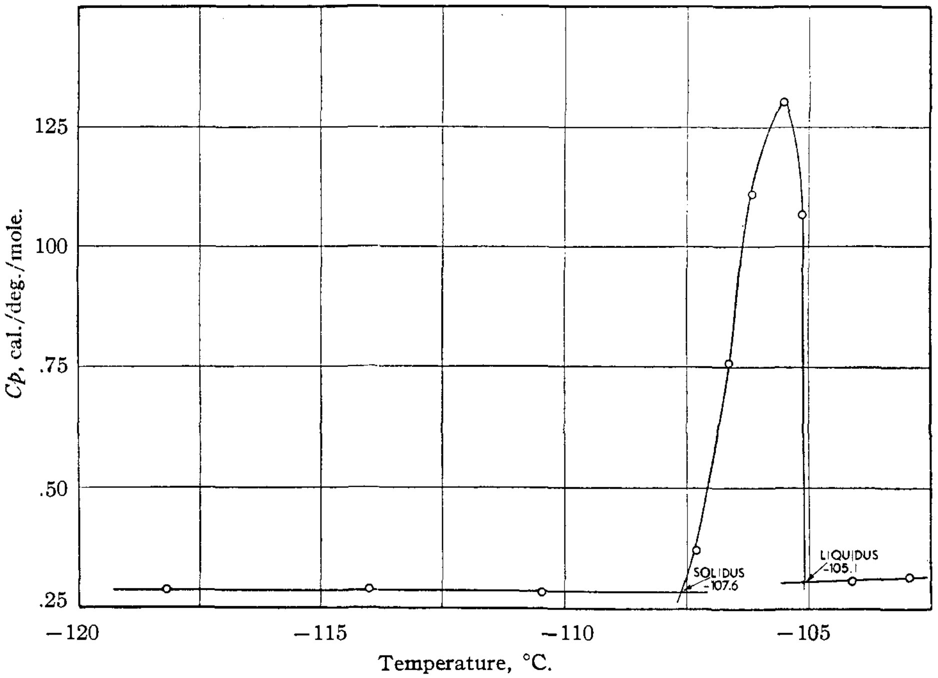

Fig. 2.—Heat capacity *vs.* temperature plot for 26.5 mole per cent. of 2,3-dimethylbutane, 73.5 mole per cent. 2,2-dimethylbutane mixture.

Due to the small absolute values, the percentage error in the heats of fusion and of the upper transition is particularly high owing to heat leaks.

Preparation of Materials. A. **Cyclopentane.**—A highly purified sample of cyclopentane was furnished us by Professor M. R. Fenske of the Petroleum Refining Laboratory of The Pennsylvania State College. This was prepared by decomposition of dicyclopentadiene and subsequent hydrogenation of the cyclopentadiene formed, followed by fractionation through an eighty-plate column. The fraction used was found to be 99.99 mole per cent. pure from its melting curve. From the data on this sample, the melting point of pure cyclopentane was found to be −93.46°.

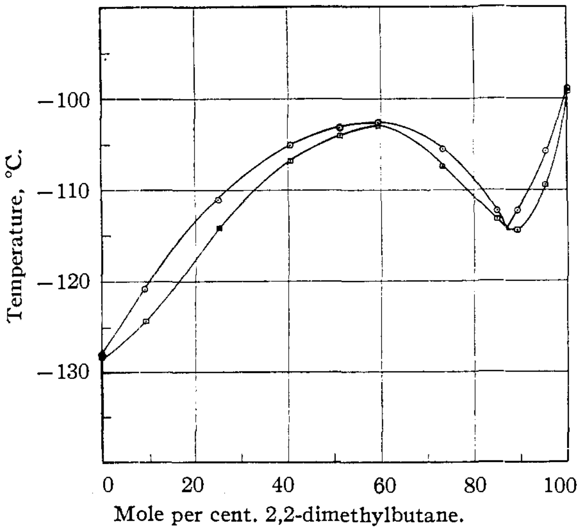

Fig. 3.—2,2-Dimethylbutane-2,3-dimethylbutane phase diagram.

B. **2,2-Dimethylbutane and 2,3-Dimethylbutane.**—These materials were prepared by Dr. E. L. Pace by hydrogenation of the corresponding olefins (furnished to us by Dr. N. C. Cook) which had been fractionated previously through a fifty-plate column. The 2,3-dimethylbutane sample was found to be 99.99 mole per cent. pure, the corresponding melting point for the pure material was −128.00°. The corresponding values found for 2,2-dimethylbutane were 99.99 mole per cent. and −98.86°.

Results

The 2,2-Dimethylbutane–2,3-Dimethylbutane Phase Diagram.—The results obtained in the system 2,2-dimethylbutane–2,3-dimethylbutane, including approximate heats of fusion, are tabulated in Table I and plotted in Fig. 3.

Table I

Equilibrium Temperatures in the System 2,2-Dimethylbutane–2,3-Dimethylbutane

Mole % 2,2-dimethylbutane	Liquidus temp., °C.	Solidus temp., °C.	Heat of fusion cal./mole
0.0	−128.00		175
9.1	−120.8	−124.2	164
25.2	−111.0	−114.2	220
40.6	−105.1	−106.8	241
51.4	−103.2	−104.0	187
59.3	−102.6	−102.9	255
73.5	−105.3	−107.6	210
84.8	−112.3	−113.2	193
89.3	−112.3	−114.4	178
95.4	−105.7	−109.4	93
100.0	− 98.86		135

In Fig. 4, curve A is a plot of the time required to reach temperature equilibrium after energy

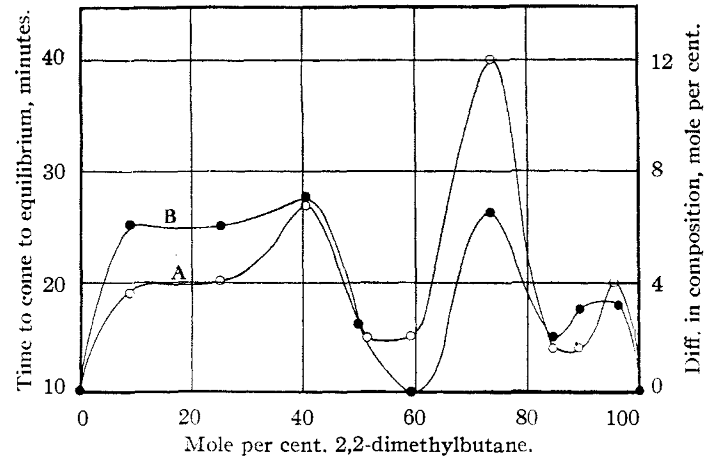

Fig. 4.—Equilibrium tests for system 2,2-dimethylbutane–2,3-dimethylbutane.

has been supplied to melt a certain fraction of the solid mixture against the composition. Curve B is a plot of the difference in composition between the solid solution and the liquid in equilibrium with it against the composition. The similarity between the shapes of the two curves illustrates that the time to come to equilibrium depends upon the difference between the composition of the liquid and the solid separating. Thus, it seems that changes must be occurring in the solid and it is likely that these represent adjustment in the solid composition as the temperature is raised which continues until the solid is in equilibrium with the liquid. The curve plotted for the solid will be the true equilibrium curve only if these adjustments are possible.

TABLE II

EQUILIBRIUM TEMPERATURES IN THE SYSTEM 2,2-DIMETHYLBUTANE–CYCLOPENTANE

Mole % cyclopentane	Liquidus temp., °C.	Solidus temp., °C.	β to γ transition temp., °C.	α to β transition temp., °C.	Heat of fusion, cal./mole
0.0	− 98.86				135
7.3	−120.9	−124.2			139
14.3	−127.4	−130.5			141
25.3	−134.7	−137.1			117
35.7	−139.3	−140.2			121
48.8	−141.7	−142.3			146
57.7	−139.8	−141.0			150
61.7	−136.3	−139.1	−139.6		132
66.2	−135.3	−136.3			194
70.1	−135.7	−138.7			200
71.9	−136.2	−139.6	−144.3	−151.0	147
73.6	−136.8	−140.3	−143.3	−151.7	69
75.1	−136.8	−142.0	−143.4	−151.9	63
76.9	−138.2	−143.8	−144.3	−152.0	54
79.2	−141.0	−144.7	−145.0	−151.9	35
81.2	−144.4	−145.7		−151.9	172
82.5	−143.2	−146.1		−151.9	197
83.8	−143.1	−146.0		−152.0	88
85.0	−142.1	−145.0		−152.0	66
86.3	−140.2	−143.0	−147.5		123
86.6	−139.8	−142.8	−147.5		86
88.3	−131.7	−136.4	−140.5	−152.1	8
89.9	−125.7	−134.5	−140.0	−151.8	21
91.9	−118.7	−126.2	−140.0	−151.9	21
94.3	−108.9	−115.0	−140.0	−152.1	23
100.0	− 93.46		−135.09[a]	−150.77[a]	144

[a] See reference 4.

Measurements were not taken to sufficiently low temperatures to include solid-phase transitions.

The 2,2-Dimethylbutane-Cyclopentane Phase Diagram.—The results obtained in the 2,2-dimethylbutane–cyclopentane system, including approximate heats of fusion, are tabulated in Table II and plotted in Fig. 5.

Because of the short time of reaching apparent equilibrium after energy additions it was not possible to apply the test used in the case of 2,2-dimethylbutane–2,3-dimethylbutane to ascertain whether the composition of all the solid was that in equilibrium with the liquid. However, the fact that the same solidus point and the same temperatures of transition (extrapolated to 100% transformed) were obtained irrespective of the rate of cooling or heating is strongly indicative of equilibrium.

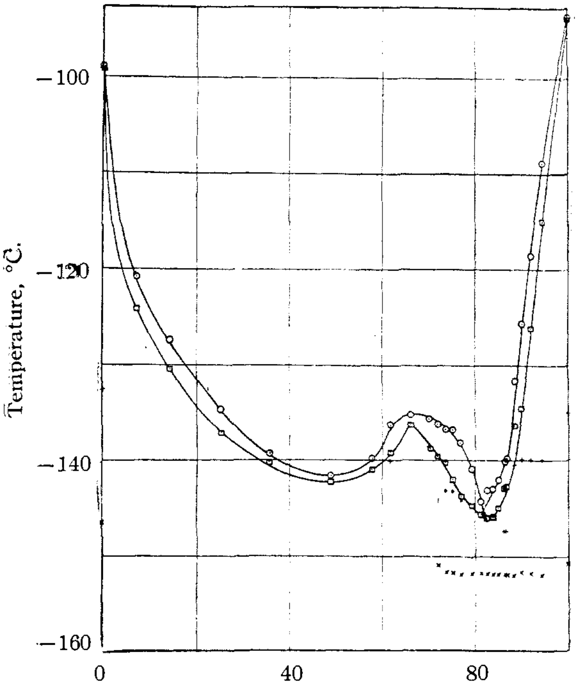

Fig. 5.—2,2-Dimethylbutane–cyclopentane phase diagram.

Although, in the mixtures, the α to β transition always occurred over a small range and the β to γ over a larger range, only the temperatures at which the transitions were complete are given in Table II and plotted in Fig. 5. Lack of sharpness of the start of transition obscured the points analogous to those on the solidus curve for the solid-liquid equilibrium. The temperatures given correspond to those on the liquidus line.

Rotational transitions were observed only for mixtures with more than 60% cyclopentane. However, the β to γ transition was missing in the region 80–85% cyclopentane. The temperature of the α to β and β to γ transitions of cyclopentane, −150.77° and −135.09°, respectively,[4] were lowered as can be seen by referring to Table II and Fig. 5.

The effect of solid soluble impurity (2,2-dimethylbutane) upon the lower rotational transition of the cyclopentane crystal can be seen from Fig. 6 and Table III where the molar heat (based on one mole of mixture) of the α to β transition is plotted against the cyclopentane composition, in the former and tabulated in the latter. In Table III, column one lists the mole per cent. cyclopentane in each mixture, column two lists the heat of the α to β transition calculated on the basis of one mole of mixture, column three lists this quantity calculated on the basis of one mole of free cyclopentane, it being assumed that the rest is combined in a complex (to be explained later), containing 67 mole per cent. cyclopentane. The heat of the α to β transition calculated on the basis of one mole of mixture, decreases until the heat disappears entirely at about 68 mole per cent. cyclopentane. In keeping with this, no evidence of a lower transition was found in the 70.1 mole per cent. cyclopentane mixtures. The reason for the calculation, taking into account the amount of cyclopentane tied up as complex, will appear presently.

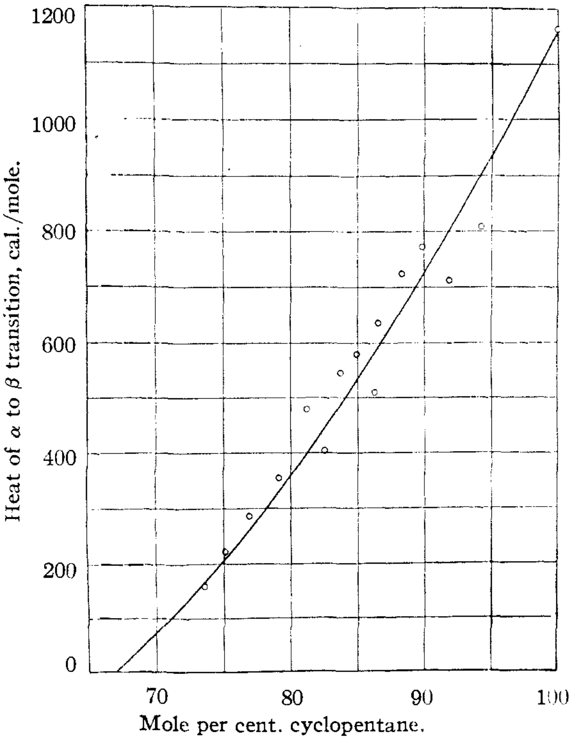

Fig. 6.—Heat of α to β transition for 2,2-dimethylbutane–cyclopentane mixture.

TABLE III

HEAT OF α TO β AND β TO γ TRANSITIONS IN THE SYSTEM 2,2-DIMETHYLBUTANE–CYCLOPENTANE

Mole % cyclo-pentane	Heat of α to β transition, cal./mole One mole mixture	Heat of α to β transition, cal./mole One mole free cyclo-pentane	Heat of β to γ transition, cal./mole One mole mixture	Heat of β to γ transition, cal./mole One mole free cyclo-pentane
61.7			55	
71.9			13	83
73.6	159	780	40	191
75.1	223	885	53	208
76.9	288	945	52	171
79.2	355	950	59	156
81.2	480	1100		
82.5	404	850		
83.8	545	1060		
85.0	580	1050		
86.3	510	865		
86.6	635	1060		
88.3	725	1115	57	88
89.9	773	1110	48	70
91.9	715	955	49	65
94.3	810	987	110	133
100.0	1165[a]		82.8[a]	

[a] See reference 4.

The effect on the upper transition can be seen from column four of Table III which lists the heats of the β to γ transition based on one mole of mixture, and from column five which lists the same quantity calculated on the basis of one mole free cyclopentane.

The low precision indicated by the scattering of the points in Fig. 6 is a result of accumulation of errors. The transition temperature was measured by adding small amounts of energy to partially transform the crystal stable at the lower temperature to the higher temperature form and then observing the equilibrium temperature. The contents of the calorimeter would require an hour or more to come to equilibrium for each energy input. As each heat of transition required some four or five energy increments, the accuracy in the heat of transition obtained by summing the energy increments is greatly reduced. The heats of the β to γ transition of the mixtures which exhibited the α to β transition were of the same order of magnitude as that for pure cyclopentane as shown by Table III; due to their small values the percentage error is high.

It was possible to super-cool the γ modification some twenty or thirty degrees below the α to β transition whence upon slowly warming, the crystal would change to the α modification. This procedure would take place over a period of four to five hours during which time the calorimeter

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[4] Aston, Fink and Schumann, THIS JOURNAL, **65**, 341 (1943).

and contents would warm until the entire material was transformed which raised the temperature to about 10° below the α to β transition.

If the supercooling were only continued to between the β to γ and α to β transitions, no evidence for the β to γ transition was noticed on warming, thus proving that it is the γ form that is supercooled. In keeping with this, the solidus and liquidus points on the super-cooled γ samples agreed with the results obtained on runs in which the α to β and β to γ transitions were obtained.

Discussion

Both phase diagrams can be considered as made up essentially of two solid solution systems. In the 2,2-dimethylbutane–2,3-dimethylbutane system, between 0 and 60 mole per cent. 2,2-dimethylbutane, where a maximum occurs, the phase diagram is one in which there is complete solid miscibility without any intermediate maximum or minimum. Between 60 and 100 mole per cent. 2,2-dimethylbutane, once again there is complete solid miscibility but the system exhibits an intermediate minimum. In the same way, the 2,2-dimethylbutane–cyclopentane diagram on either side of a maximum may be considered as being composed of two parts both involving completely miscible solid solutions, both of which exhibit an intermediate minimum. This maximum in each of these two binary systems seems to be evidence for an unpredicted *complex* whose nature is not immediately apparent.

Evidence of *complex* formation in the 2,2-dimethylbutane–2,3-dimethylbutane can be found in the values for the heat of fusion tabulated in the last column of Table I. There is a distinct maximum in the neighborhood of 60% 2,2-dimethylbutane which is the composition corresponding to that postulated for the complex. As can be seen from Table II the heats of fusion for the 2,2-dimethylbutane–cyclopentane system reach a maximum at about 70 mole per cent. cyclopentane which is close to the composition postulated for the complex.

The apparent maxima and minima in the heat of fusion at higher percentages of cyclopentane may well be due to the occurrence of the β to γ transition along with the fusion process. It is to be noted that in the region of from 81 to 86 mole per cent. cyclopentane, the heats of fusion are unduly large in comparison with the values on either side. This, however, is the region in which the β to γ transition does not appear. It can be seen from the diagram that it would be expected to occur at temperatures close to where the solid and liquid are in equilibrium. The heat of this transition for pure cyclopentane is 82 calories.

Therefore, it is believed that either (a) the fusion observed is that of the β form rather than the γ so that the heat effect is the sum of the transition and normal fusion or (b) that the β to γ transition and fusion occur so close together that they cannot be separately identified and therefore have been treated as fusion alone.

In the 2,2-dimethylbutane–cyclopentane diagram, the effect of solid solution on the heats of the α to β and the β to γ transitions is quite different. Within the experimental error, there is no significant change in the magnitude of the heat of the β to γ transition calculated on the basis of one mole of mixture. The temperature of that particular transition has been lowered considerably as shown by column four in Table II. Should any doubt have existed as to the existence of solid solution between these two compounds, the fact that this β to γ transition temperature was lowered 3 to 8° would be sufficient proof.

In the case of the α to β transition, the lowering is of the order of one degree, which indicates that there was solid solution persisting even in the β phase. In contrast to the β to γ transition, the magnitude of the heat effect of the α to β transition is quite sensitive to the composition. Within the experimental error, the heat of transition α to β calculated on the basis of one mole of mixture decreases linearly with increasing 2,2-dimethylbutane concentration, approaching zero in the region of 67 mole per cent. cyclopentane.

Assuming the complex to have the composition 67 mole per cent. cyclopentane, the heats of this transition calculated on the basis of one mole of free cyclopentane (see Table III, col. 3) are essentially constant within the relatively large experimental error mentioned above. It is quite probable that this constancy is significant and if so is a strong indication of the existence of the complex. The heats of the β to γ transition calculated on the same basis are difficult to interpret because of the large experimental error in this small quantity. No explanation has been found for the fact that neither the α to β nor the β to γ transitions were found with mixtures containing less than 61 mole per cent. cyclopentane.

Acknowledgment.—The authors wish to express their appreciation to Mr. N. D. MacAllister and Mr. L. R. Fruit for assisting with the measurements of the 2,2-dimethylbutane–cyclopentane system.

Summary

1. Liquid–solid equilibrium phase diagrams have been determined for the systems 2,2-dimethylbutane–2,3-dimethylbutane and 2,2-dimethylbutane–cyclopentane.

2. Each system forms a series of continuous solid solutions containing a maximum in the diagram which has been called a *complex*.

3. For the system 2,2-dimethylbutane–cyclopentane the upper and lower transition temperatures (extrapolated to 100% transformed) have been determined over the range of composition where the transitions occurred as well as the heats of transition and fusion.

4. The lower transition is found only for the pure components and mixtures having composi-

tions between 70 and 100 mole per cent. cyclopentane, while the heat of this transition per mole of mixture decreases from 1165 cal. at 100 mole per cent. cyclopentane to 0 cal. at approximately 68 mole per cent. cyclopentane.

5. The upper transition is found only for the pure components and mixtures between 60 and 100 mole per cent. cyclopentane.

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The Magnetic Anisotropy of Coronene, Naphthazarin, and Other Crystals

BY MAX T. ROGERS[1]

The magnetic constants of crystals have recently proved to be a useful aid in crystal structure analysis,[2] and the magnetic constants of molecules, which can in many cases be derived from those of the crystal, are of interest theoretically. A semi-classical theory of the magnetic anisotropy of aromatic hydrocarbons has been developed by Pauling,[3] and a molecular orbital treatment by London[4]; these agree satisfactorily with experiment for most molecules for which data are available for comparison, but predict widely different values for coronene.[5] A study was therefore made[6] of the magnetic constants of coronene, both to provide experimental data for comparison with theory, and to aid in the determination of the crystal structure. Since these measurements were made, however, a complete analysis of the crystal structure of coronene has been reported[7]; the orientation observed experimentally for the molecules in the crystal is in good agreement with the prediction made from the magnetic data.

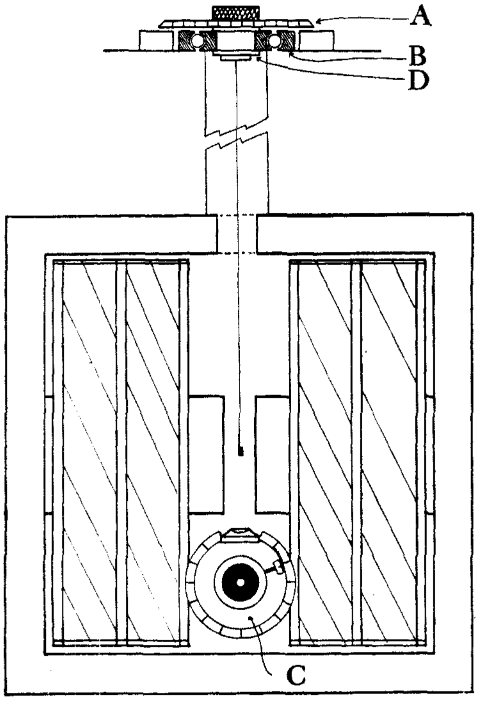

Fig. 1.—Apparatus for measurement of the magnetic anisotropy of crystals: detail of part C shown in Fig. 2.

The data for other crystals studied at the same time are also reported and discussed here.

Experimental

Apparatus.—Measurements of crystal anisotropy were made by a method developed by Krishnan[8]; the apparatus is shown in Figs. 1 and 2. The crystal was attached to a fine glass thread about 1 inch long by means of a minute amount of glyptal; when necessary this was done in an optical goniometer so that the orientation with respect to the fiber axis could be accurately determined. The glass thread was in turn attached to the lower end of a fine quartz fiber (3-7 μ in diameter[9]) about a meter long. The upper end of the fiber is attached to the pin of a torsion head. The torsion head consisted of a ball bearing (B of Fig. 1), the outer part of which was fixed, while the central part had a 360° protractor attached to it above, and the quartz fiber below. For convenience in handling and centering, the pin to which the fiber was attached was set in a brass disc (D, Fig. 1) which was held to the bearing only by a thin layer of wax. The crystal was suspended centrally between the plane parallel pole pieces (3

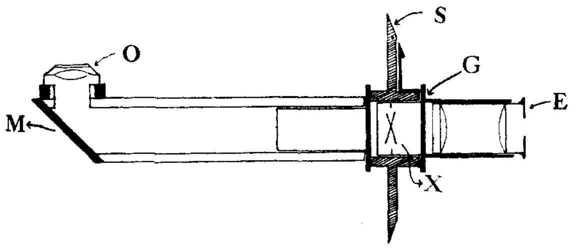

Fig. 2.—Viewing device.

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[1] Present address: Kedzie Chemical Laboratory, Michigan State College, East Lansing, Michigan.

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[9] For preparation of fibers see Strong, "Procedures in Experimental Physics," Prentice-Hall, Inc., New York, N. Y., 1938.