is approximately equal to the rate of dehydration to butylene in the absence of benzene.

4. Boron trifluoride catalyzes the alkylation of toluene by cyclohexyl fluoride but not by cyclohexyl bromide.

The Heat Capacity and Vapor Pressure Hysteresis in Liquid Isopentane. Isomers Due to Hindered Rotation

BY J. G. ASTON AND S. C. SCHUMANN

The appearance of apparent hysteresis in the heat capacity of liquid ethylene dichloride[1] has been attributed by Railing to hindered rotation but the interpretation has been questioned by Pitzer somewhat arbitrarily.[2] The presence of isomers due to hindered rotation will manifest itself when the minima are unequal and the barrier height large due to any of the possible causes. In most aliphatic compounds the barriers will be small enough for equilibrium to be attained at ordinary temperatures. The equilibria, as lower temperatures are approached, will be characterized by decreasing proportions of the isomers of highest energy. Rapid cooling, therefore, will yield a liquid which will approach equilibrium from the side of excess of the isomer of higher energy. The isomer of higher energy will have a configuration of greater repulsive forces (assuming the barriers to be due to repulsion). Such a configuration corresponds to higher force constants and therefore higher frequencies, and, other things being equal, will lead to lower heat capacities than those of the form of lower energy. The non-equilibrium mixture obtained by rapid cooling, therefore, should have lower heat capacities than the equilibrium mixture. A rapidly heated equilibrium mixture will approach equilibrium from the side of excess of the form of *lower* energy. Thus, more heat will be taken up for the heating than required by the equilibrium mixture, and this heat would be re-emitted as equilibrium was reached, producing warmer drifts of a calorimeter accompanying heat capacities *higher* than normal.

A non-equilibrium mixture, as identified by its heat capacity, might be expected to manifest differences in vapor pressure from those of the equilibrium mixture. *We have been able to demonstrate such a hysteresis in the vapor pressure of liquid isopentane and have proved it to be experimentally real.*

Heat Capacity Hysteresis.—Figure 1 is a graph of heat capacities obtained on the liquid in adiabatic calorimeter, B. The legend to the points in Fig. 1 also gives a complete history of the cooling of each. The diameter of the circles and the length of side of the squares is five times the experimental precision (0.06%).[3] Figure 1 shows a general agreement with the above predictions about the heat capacities of non-equilibrium mixtures of isomers due to restricted rotation. One particular feature of Fig. 1 requires comment. Series B, D and H were taken on a sample after it had been distilled into the calorimeter sufficiently slowly to produce equilibrium conditions as shown by the subsequent behavior, while Q and T were slowly cooled and are therefore also on a mixture which has reached equilibrium. At the lower temperatures these points approximate those of non-equilibrium mixtures, but rapidly deviate from the non-equilibrium curve as the temperature increases. Series H goes to the lowest temperatures and one might assume that its heat capacity curve merges into that of the *non-equilibrium* mixture due to some phenomenon characteristic of the degrees of freedom involved. It is then necessary to explain why all the other series (B, D, Q, and T) have a different temperature at which the divergence occurs. It is to be noted that, in general, the series which has spent longest at lower temperatures branches off at lower temperatures than in the case of any other run. We believe that this is due to the fact that the series was rapidly heated to the sensitive region prior to taking heat capacities. In this way a mixture was produced which was superheated, thereby keeping the low temperature ratio of isomers which is

(1) Railing, THIS JOURNAL, **61**, 3349 (1939).
(2) Pitzer, *ibid.*, **62**, 331 (1940).
(3) Aston and Eidinoff, *ibid.*, **61**, 1533 (1939).
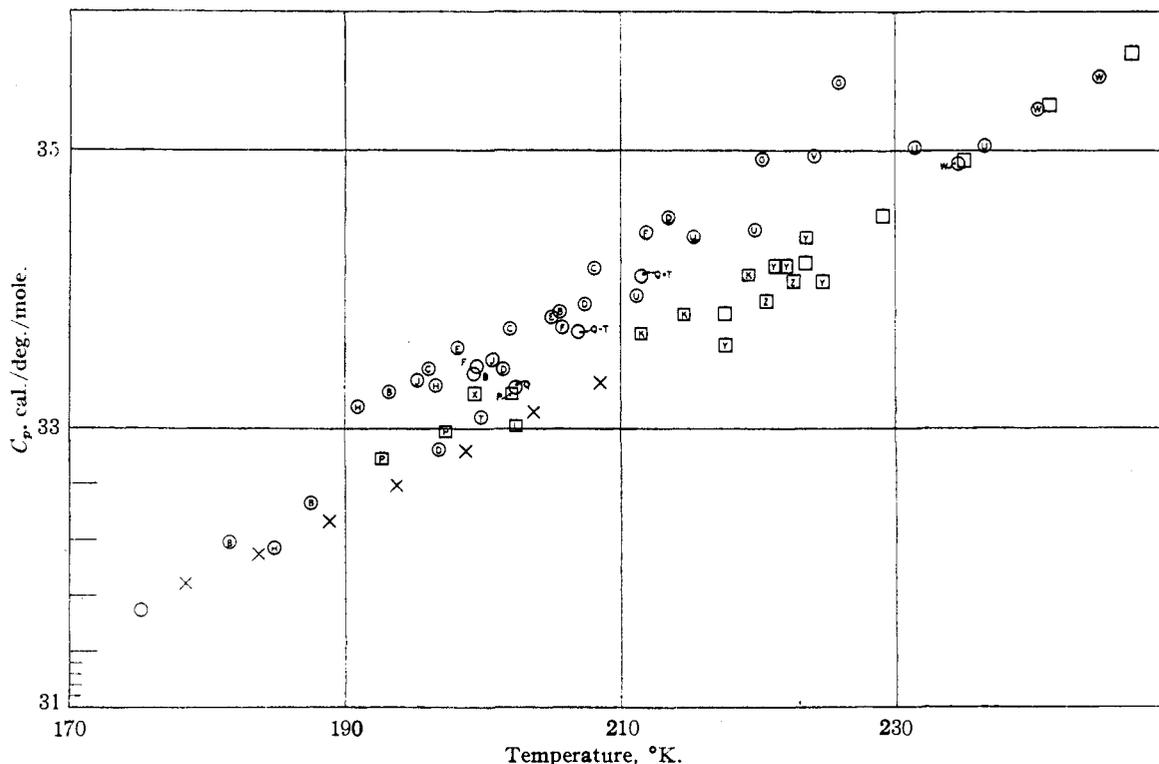
Fig. 1.—The heat capacity of liquid isopentane from 170 to 250°K.

Samples: O, □, ×, record uncertain; (A), sample distilled in at about 210°K., cooled rapidly to 60°K., and after standing at 60°K. for four hours, points were taken on the solid; (B), sample then slowly heated from 90°K.; (C), sample then slowly heated from 120°K.; (D), next cooled quickly from 200 to 110°K., melted and quickly heated to 185°K.; (E), then stood between 170–210°K. for two days; (F), then stood between 170–210°K. for one day; (G), then stood between 170–210°K. two days; (H), then stood between 170–210°K. for nine days; (I), then stood between 140–190°K. for two days; (J), then stood between 140–190°K. for one day; [K], finally heated rapidly to 15°C., cooled immediately to 220°K., then stood three days between 180–200°K ; [L], then stood between 180–210°K. for four days; [M], then cooled rapidly from 200°K., frozen slowly, then points taken on solid; [N], then stood at 90°K. for one day, then point taken on solid; [P], then stood at 90°K. for one day, then melting point taken after which stood at 120°K. for one day, then heated rapidly to 190°K.; (Q), finally heated rapidly to 15°C., then cooled slowly (over eighteen hours) to 200°K.; (R), then cooled rapidly to 90°K., stood for one day, then points taken on solid; (T), then stood two days at 90°K., then melting point taken after which stood one day at 120°K., then rapidly heated to 195°K.; (U), then stood sixteen days between 150–200°K.; (V), then stood two days between 210–225°K.; (W), finally stood two days between 215–230°K.; [X], cooled rapidly (eight hours) to 170°K., then heated to 200°K.; [Y], then cooled to 185°K., heated to 220°K., and finally stood between 215–230°K. for five days; [Z], stood one hour at 220°K.; (II), vapor pressures while distilling sample from calorimeter (points on solid appear in Fig. 1 of the following paper).

richer in the low energy form than the true equilibrium mixture for the new temperature. This would give rise to higher heat capacities and explain the branching upward as due to lack of equilibrium *from the low side*. The tendency to revert to equilibrium is balanced by the effect of heating in each heat capacity measurement which requires further change to establish an equilibrium corresponding to the new conditions. It is not possible to go further than such a qualitative explanation of these heat capacity curves.

Hysteresis in the Vapor Pressures.—Figure 2 shows a graph of $\log_{10} P$ *versus* T for the heat

capacity runs in which the vapor pressure was observed simultaneously. The points are lettered to correspond to the points of Fig. 1. The data are listed in Table I. The runs which gave high heat capacities gave high vapor pressures. The precision in the vapor pressure measurements is about 0.006 mm. corresponding to one-tenth of the diameter of the circles or length of side of the squares. The difference between the curve through the "equilibrium points" and the non-equilibrium ones is about 0.8 mm. at the high pressures and about ten per cent. of the pressure at all pressures. In Fig. 2 is included a line repre-
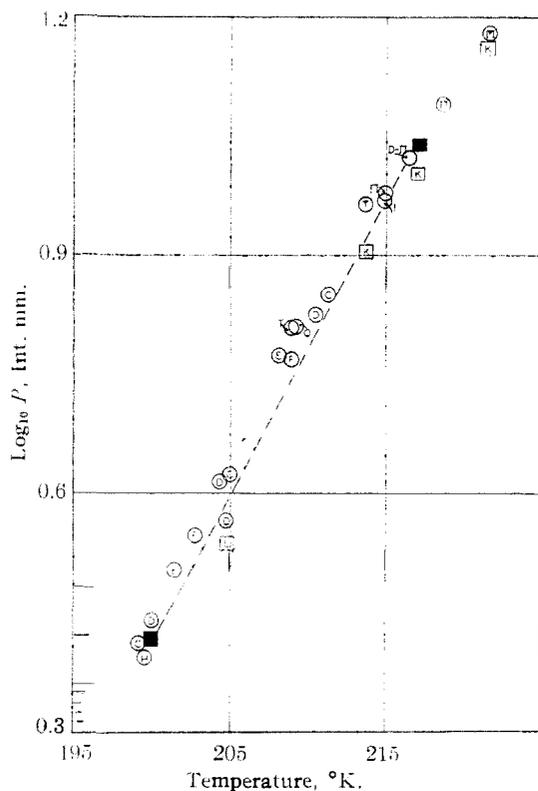
Fig. 2.—The vapor pressure of liquid isopentane from 195 to 225°K.

TABLE I

VAPOR PRESSURE DATA

Date	Cut legend	T, °K.	P, int. mm.
Oct. 12	C	199.096	2.58
		204.960	4.21
		211.282	7.06
Oct. 14	D	200.043	2.76
		204.283	4.12
		210.484	6.19
		216.532	10.55
Oct. 16	E	201.390	3.19
		208.092	5.44
Oct. 17	F	202.727	3.52
		208.892	5.86
		214.913	9.28
Oct. 28	H	187.330	0.74
		193.618	1.44
		199.471	2.48
Nov. 4	K	213.749	8.00
		217.057	10.52
		221.496	14.84
Nov. 8	L	204.784	3.44
Nov. 17	Q	204.737	3.69
		209.220	6.47
Nov. 22	T	208.917	6.44
		213.729	9.18
Dec. 19	II	215.003	9.30
		216.611	10.55
		218.730	12.31
		221.669	15.14

■— — —■   Vapor pressure equation.

senting the vapor pressure equation derived from measurements taken before the hysteresis phenomenon was discovered, without simultaneous heat capacity measurements, and under conditions such that no cooling history is known. It is seen that differences in cooling rate produce effects on the vapor pressure over 100 times the precision of our measurements.

Abnormal Energy Emission.—Abnormal drifts were observed in the after period of heat capacity measurements on the samples that had been slowly cooled. The drifts were always toward higher temperatures and were greater than the usual ones which could be accounted for quantitatively, by heat leak due to the warmer shield top. They persisted long after thermal equilibrium had been established in the calorimeter (*i. e.*, after ten minutes). These drifts indicate an abnormal emission of energy of about 0.03 calorie per minute with 0.4 mole in the calorimeter. Such a behavior would be expected if the conditions of the equilibrium at the lower temperature were adjusting themselves to those of the higher as discussed above. For want of a better procedure, the total drift was used without

regard to cause, in the extrapolations required in the correction for heat leak. Thus, in fact, the high heat capacities do correspond to lack of equilibrium, *as approached from the low temperature side*, in samples cooled sufficiently slowly to be in equilibrium initially.

The possibility was considered that the hysteresis effects may have been due to the condensation of a very viscous liquid in the filling tube. This possibility was eliminated by consideration of the geometry and temperature control of the apparatus[3] in relation to the magnitude of the effects observed.

In the middle of the measurements the calorimeter was emptied and found to be in perfect working order by measuring its heat capacity at two temperatures. Immediately after completion of the measurements of this paper, heat capacity measurements were made at seven temperatures on dimethyl ether and found to agree with those taken in calorimeter C[4] within an average devia-

(4) Kennedy, Sagenkahn and Aston, THIS JOURNAL, **63**, 2267 (1941), see Fig. 1 in which the blackened circles are those taken with the adiabatic calorimeter B, a statement omitted due to oversight.

tion of 0.35%. The curve drawn through the results obtained with calorimeter B lay 0.3% above the curve obtained with calorimeter C. Since the mean deviation of the results with the present calorimeter (B) from the curve through them was less than 0.05%, the results with it are probably the more accurate. Likewise, heat capacity measurements on cyclopentane[5] subsequent to those of dimethyl ether, showed no erratic behavior and agreed with those of Jacobs and Parks[6] within their experimental error which is greater than our own.

Experimental

Preparation and Purification of Isopentane.—The sample was kindly prepared for us by Professor M. R. Fenske and co-workers.[7] It was obtained by fractionating a cut from a straight run petroleum solvent through a column of approximately 100 theoretical plates, with subsequent refractionation through a very efficient low temperature column to eliminate possible traces of n-butane. Two hundred cc. of the final distillate boiled within 0.02°. About 45 cc. of the middle cut of this distillate was dried over phosphorus pentoxide, deaerated and distilled into the calorimeter. The sample thus obtained was later found to contain 0.005 mole per cent. of liquid-soluble, solid-insoluble impurity as estimated from the melting point range.

The Apparatus and Heat Capacity Measurements.—The method, temperature scale and accuracy were as described before.[3,8] One defined calorie was taken equal to 4.1833 international joules. In correcting for the material vaporized into the filling line, the available data for the density of the liquid[9] and the vapor pressure results described later were used. In all cases the molecular weight of isopentane was taken to be 72.146.

The calorimeter was usually at "equilibrium" after eight to ten minutes. After the calorimeter had reached "equilibrium," readings were generally taken for ten minutes or so, in order to determine the drift rate for the small heat leak correction necessary because of the slightly warmer shield top. However, on several occasions where so-called abnormal drifts were obtained, readings of the calorimeter temperature were continued till one hour after the heating period. The drift rate at this time, in every case, did not appreciably differ from that shortly after "equilibrium," which was used in calculating the heat leak.

The Vapor Pressure Measurements.—These were taken after the apparatus had come to "equilibrium" in the after period of heat capacity measurements. The conditions were such that no heat was being gained or lost by the calorimeter, the absolute temperature being determined

on the resistance thermometer. The difference in mercury levels was measured by a Société Génévoise cathetometer which could detect differences of 0.001 mm. The vapor pressures were so small that only the micrometer eyepiece on one of the telescopes was used, with a consequent increase of precision due to the elimination of the readings on the standard meter.

Discussion

In the next paper it is shown that a potential barrier of about 8000 cal./mole hinders the internal rotation of the ethyl group with respect to the isopropyl group in isopentane. This corresponds to a value of $S_f - S$ of 2.38 cal./deg./mole for the amount by which the free rotational entropy is decreased. It is natural to assume that essentially free rotation exists in the activated state involved in the change of one form to the other. Since this state is that in which the degree of freedom has an energy greater than 8000 cal., the entropy of it will be that corresponding to free rotation for the degree of freedom under discussion (to the degree of approximation involved in including the first fifty rotational states which do not correspond to activation).

The specific rate constant for the change of one form of the molecule to the other is then[10,11]

$$k_i = \kappa \frac{kT}{h} e^{\Delta S*/R} e^{-\Delta H*/RT} \qquad (1)$$

with $\Delta H*$ equal to 8000 and $\Delta S*$ equal to 2.38 cal./deg. Eyring[11] has deduced that for the change of a *cis* to a *trans* olefin κ is of the order of 10^{-7}. For want of the proper one, substituting this value in (1), k_i turns out to be 10 sec.$^{-1}$ at 240°K. which is barely consistent with the experimental evidence that the process of change of one of the forms of isopentane to the other is sufficiently slow to allow isomers to exist for a reasonable period below 240°K.

In the next paper values of the melting point of isopentane are reported. The melting point was taken on a solid which melted to a liquid of low heat capacity (points P in Fig. 1) and on a solid which yielded a liquid of high heat capacity (points T in Fig. 1). The results of both series of values were the same. This fact appears to conflict with the above explanation of the hysteresis phenomenon but can be explained away. The freezing point constant ($RT^2/\Delta H_f$) is 20.6. This would indicate possible changes of the order of 2° in the *freezing point* due to changing amounts of isomers assuming no solid solution. Moreover,

(5) Aston, Schumann, Fink and Doty, THIS JOURNAL, **63**, 2029 (1941).

(6) Jacobs and Parks, *ibid.*, **56**, 1513 (1934).

(7) We should like to thank Professor M. R. Fenske and Messrs. S. Lawroski, R. W. Benoliel, R. H. McCormick and A. E. Schubert for their generosity in supplying us with this material.

(8) Aston, Eidinoff and Forster, THIS JOURNAL, **61**, 1539 (1939).

(9) "International Critical Tables." McGraw-Hill Book Company, New York, N. Y., 1926.

(10) Eyring, *Chem. Rev.*, **17**, 65 (1935).

(11) Magee, Shand and Eyring, THIS JOURNAL, **63**, 679 (1941).

the effect of one isomer on the other might be expected to produce premelting of different degrees in the two cases. The absence of appreciable premelting in both cases means that both solids are solid solutions or mixtures close to the eutectic composition.[12]

If both forms had the same melting point in the pure state, perfect solid solutions would have the same melting point at all compositions. With a mixture close to the eutectic composition, what was really the eutectic point would be taken as the melting point, and in the absence of impurity a constant temperature would be maintained until all of one form had gone into the liquid of the eutectic composition, leaving the other form in excess. The excess of the other form would melt (or dissolve in the liquid) as the temperature rose, the process being complete at the freezing point of the mixture of forms. This latter process would produce an increase in the heat capacity with a peak near the freezing point. With mixtures close to the eutectic composition, this peak could escape detection. However, it is impossible that the mixtures range in composition from one to the other side of the eutectic point since in this case high heat capacities would result from both slow and fast cooling. That the different series of vapor pressure measurements have different slopes over the range of high heat capacities shows that a saturated solution of one of the forms is not involved. Such a situation would

yield only one vapor pressure curve over the range of the two phase systems which is necessarily one of higher heat capacity. This vapor pressure curve would end at the freezing point which would vary according to conditions of cooling, the vapor pressure curve above this point being discontinuous with that below and also variable according to conditions of cooling. Thus it is difficult to imagine a eutectic phenomenon, involving any pair of solid phases, being involved in the observed hysteresis.

Summary

1. An exhaustive study of the heat capacity of liquid isopentane has been made in the range 180 to 240°K. with a precision of 0.06%.

2. Hysteresis in the heat capacity has been found for the liquid in this region to a degree one hundred times the precision of measurement.

3. Simultaneous vapor pressure measurements exhibit hysteresis effects of about 100 times the precision of measurement.

4. The results have been considered as possibly due to the slow transfer of one into the other of the isomeric forms made possible by restricted rotation.

(12) If far away from the eutectic composition the eutectic phenomenon would be like that in a system with a low percentage of soluble impurity where it appears as a peak in the heat capacity curve for the solid at the eutectic point. This peak is the start of premelting which causes the heat capacity to be increasingly raised thereafter.