

## TEMPERATURE DEPENDENCE OF INTERMOLECULAR ACTIVATION ENERGY FOR FLOW IN LIQUIDS AND SOLUTIONS

### Part II.—Preliminary Application of the Ideas of Domain Structure to the Energy Jumps Observed in Ethylene Glycol

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A preliminary account is given of the possible application of theories of first and second order transitions to discontinuities in activation energy of flow observed in several di-hydroxylic liquids. It is shown that the specific heat data for ethylene glycol ( $\text{CH}_2\text{OH}$ )<sub>2</sub> are consistent with the idea that the extra change in internal energy due to molecular association or ordering over the range 28° to 68°C. is about one half of the change in flow activation energy over the same range.

Assuming that the molecular ordering corresponding to each jump in activation energy is similar in effect to the well known order  $\rightleftharpoons$  disorder transitions for magnetism and for alloys like  $\beta$ -brass, an estimate can be made of the height of the anomalous specific heat peaks to be expected. This comes out to be of the order of 0.01 cal./g./°C. for ethylene glycol, which would not be readily observed by conventional calorimetry, but is well within the power of microcalorimetric methods.

#### 1. Basic Considerations

This communication gives a preliminary account of the possible application of theories of first and second order transitions to the sharp discontinuities in activation energy,  $\epsilon$ , and the level-structure found experimentally in the di-hydroxylic liquids, ethylene glycol,<sup>1,2</sup> ( $\text{CH}_2\text{OH}$ )<sub>2</sub>, and water,<sup>3</sup> both shown in Fig. 1, (solid circles) and later in mixtures of water and ethyl alcohol,<sup>4</sup> cf. Fig. 1, middle curve (hollow circles). These discontinuities open up speculation regarding the possibility of a series of latent heat steps or else specific heat anomalies, of a magnitude related to the depths of the discontinuities in the activation energy graphs. If we consider that these discontinuities result from a partial breakdown or other change of the regular structure of the molecular aggregates in these hydroxylic liquids, of which an extreme form would be the splitting of an aggregate into two smaller ones, we can make the reasonable assumption that the potential energy absorbed by the aggregate on becoming 'disordered' is a fraction, say one-half, of the change in activation energy,  $\Delta\epsilon$ , between adjacent aggregates in flow. It then follows that the graphs of Fig. 1 should with the sign of  $\epsilon$  reversed give a measure of the internal energy changes due to varying association within the liquid as the temperature is varied.

Quantitatively, we can see that the total internal energy change due to association when estimated in this way from Fig. 1 is consistent with

the specific heat data for ethylene glycol. Thus, in going 40 degrees from 28°C. to 68°C., we have

$$\Delta(E/R) = \Delta(\epsilon/k) = 1000 \times (2.96 - 3.56) = -600 \text{ cal./mole.},$$

whence

$$\Delta U = -\frac{1}{2} \Delta E \approx -\frac{1}{2} R \times (-600) = 300 \text{ cal./mole.} \quad (1)$$

which would correspond to an average specific heat contribution of  $600/40 = 15 \text{ cal./}^\circ\text{C./mole}$ , i.e.  $0.24 \text{ cal./g./}^\circ\text{C.}$  This constitutes over one-third of the observed specific heat of glycol, viz.  $0.58 \text{ cal./g./}^\circ\text{C.}$ , and bears comparison with the difference of  $0.16 \text{ cal./g./}^\circ\text{C.}$  between the specific heats of ethylene glycol and the non-hydrogen-bonded benzene (0.42). The situation is not so clear when one considers the individual energy changes associated with each jump  $\delta E/R = \delta\epsilon/k$  in Fig. 1; this works out to be of the order of

$$\begin{aligned} \delta U &= -\frac{1}{2} \delta E = -\frac{1000}{2} R \times (-0.08) = 80 \text{ cal./mole} \\ &= 1.3 \text{ cal./g.,} \end{aligned} \quad (2)$$

for glycol in the temperature range of 28°C. to 68°C. This is such a sizeable quantity if given out as a latent heat (at just one temperature) as to make it unlikely that it could have escaped detection thus far. One is therefore led to consider a mechanism whereby this change  $\delta U$  would be spread out over a considerable temperature interval, thus producing a relatively much smaller specific heat peak.

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## 2. The Ordered Domain Approach

In discussing the experimental data for flow activation energy of dilute aqueous ethyl alcohol in Part I of this series,<sup>4</sup> it was noted that the step-like transition from one energy value to the next in a hydroxylic liquid can be thought of as similar in character to the well-known ferromagnetic  $\rightleftharpoons$  paramagnetic transformation or the order  $\rightleftharpoons$  disorder changes observed in several alloy systems, e.g.  $\beta$ -brass, copper-gold, silver-zinc. The presence of any one type of regular domain in a substance produces a definite critical transition temperature,  $T_c$ , below which the domains are more or less completely ordered, while above it there is randomness of arrangement within the domain.

Since the mechanism of single order  $\rightleftharpoons$  disorder (super-lattice) transitions is well understood in solids according to the Bragg and Williams

theory,<sup>5</sup> we first consider for simplicity the case of a hypothetical liquid showing an *isolated* discontinuity in activation energy (Fig. 2(a)). Associated with this, there will presumably be (long - range) ordering of some sort that disappears fairly sharply (Fig. 2(b), thick line for Bragg and Williams order parameter,  $S$ ) at the critical transition temperature,  $T_c$ , and it is plausible that the internal energy variation connected with the single jump of Fig. 2(a) will also follow a similar curve; the slope of the ideal curve will be closely related to the anomalous specific heat, cf. the thick full line in Fig. 2(c). However, the short-range order<sup>5,6</sup> between close neighbours will change rather more gradually on passing through the transition temperature, as shown schematically by the broken line in Fig. 2(b). Since this short-range order determines the nearest neighbour interactions important for the internal energy, the corresponding derived specific heat curve is more the sort of effect to be found experimentally, cf. the anomalous specific heat curve

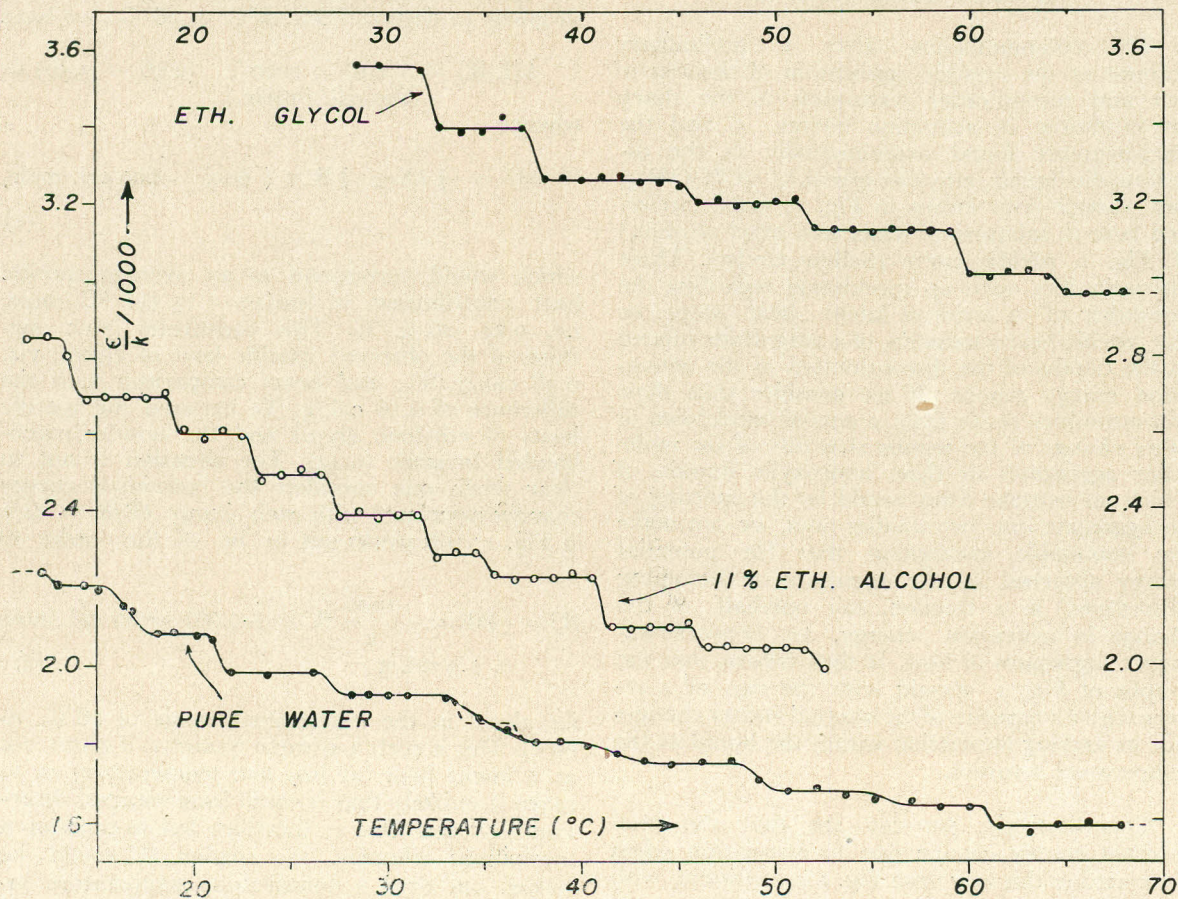


Fig. 1.—Graphs showing the series of sharp jumps observed in the (previously published) activation energy  $\epsilon$  for (i) pure water (lowest curve), (ii) pure ethylene glycol (top curve) and (iii) 11% aqueous alcohol (middle curve, hollow circles). The ordinates are  $(\epsilon/k)/1000 = (E/R)/1000$ , thus giving kilocalories/mole  $\times \frac{1}{2}$ . The broken line step at 35°C. in the graph for water indicates the extra step found when measurements were taken with an interval  $\Delta T = 1$  deg. C.

for  $\beta$ -brass shown by the broken line in Fig. 2(c).

It is seen from Fig. 2 that about half of the change in the internal energy (and the order parameters) occurs in a temperature range of  $\delta T = T_c/10$ , which can thus be used as a sort of 'half-width' of the anomalous specific heat peak. It follows that in a search for such an effect, the peaks to be looked for would be of the order of

$$\begin{aligned} \delta U/\delta T &\approx \frac{1}{2}\delta E/(T_c/10) = 5\delta E/T_c & (3) \\ &\approx 800/T_c = 2.5 \text{ cal./mole/}^\circ\text{C. from eq.2} \\ &= 0.04 \text{ cal./g./}^\circ\text{C.,} \end{aligned}$$

which appears simple to detect by ordinary calorimetry, as in the case of alloys, where the height of the  $c_p$  peak is about 0.1 cal./g./ $^\circ\text{C.}$  above the normal specific heat.

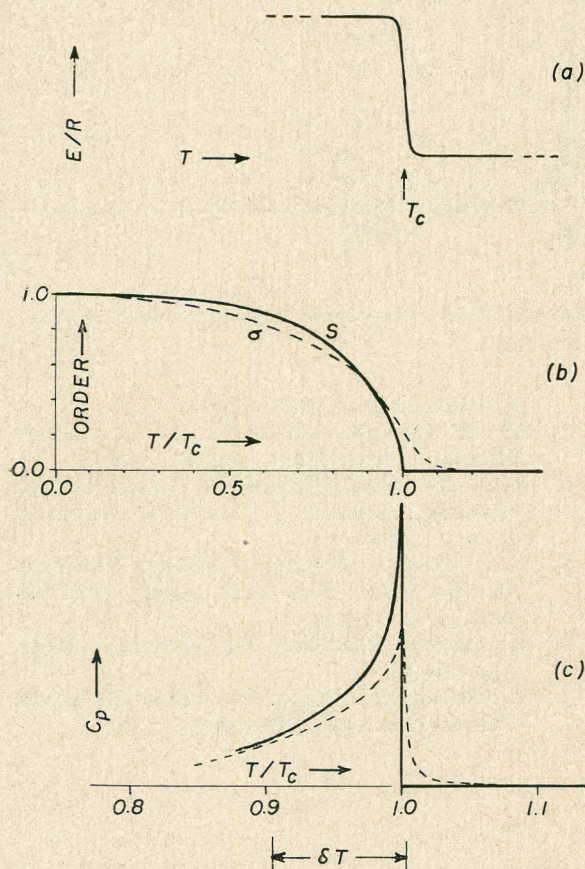


Fig. 2.(a)-(c).—Correlation of a single energy jump, represented schematically at (a), with the temperature variation of order parameters, shown in (b) from  $T/T_c=0$  to about 1.2, and with Fig. 2(c), showing the corresponding anomalous specific heat variations associated with the ordering in crystalline materials. Solid lines for long-range order, while the broken line curves take account of short-range order, in Figs. 2(b) and 2(c).

### 3. Influence of Close Sequence of Discontinuities

In the actual case of ethylene glycol and similar liquids, on the other hand, one is faced with the (probable) existence of a more or less regular sequence of transitions corresponding to the steps observed in Fig. 1. While it may, to a first approximation, be assumed that the various transitions do not have an appreciable physical interaction, they will nevertheless combine to increase the "background" specific heat at the peak corresponding to any one transition and to diminish the height of the peak above this. The magnitude of this effect is considerable when the interval  $\delta_1 T$  between the peaks is much less than the half-width  $\delta T$  for each peak, and can be estimated as shown in Fig. 3, where  $\delta_1 T = \delta T/3$ .

If we fix our attention on the middle peak P in the bottom half of Fig. 3, it is readily seen that only the central portion of the peak extending over the range  $\delta_1 T$  should be observed in the final summation. However, the background due to the neighbouring peaks is seen in the graphical summation at the top of Fig. 3 to produce a further change of shape tending to make the peak more nearly symmetrical, and the net result is that the heights of the peaks (above the background) are diminished by a factor of about  $\delta_1 T/(\frac{1}{2}\delta T) = 20 \delta_1 T/T_c$ . Using equation (3), we finally get for the peak heights,

$$\begin{aligned} 5\delta E/T_c \times 20\delta_1 T/T_c &= \frac{100\delta_1 T}{T_c} \times \delta E/T_c & (4a) \\ &\approx 1.8 \delta E/T_c & (4b) \end{aligned}$$

for  $\delta_1 T = 6^\circ\text{C.}$  and  $T_c \sim 320^\circ\text{C.}$  Using the numerical value of  $2 \times 80$  cal./mole for  $\delta E$ , this finally leads to a figure of 0.8 cal./mole/ $^\circ\text{C.}$  for the observable peak height, which corresponds to 0.012 cal./g./ $^\circ\text{C.}$  This is close to the limit of measurement with ordinary calorimetric methods, and would moreover be masked by the normal technique of using large measuring intervals and smoothing the data. However, specific heat variations of this order are well within the power of differential micro-calorimetric methods, which can measure down to a fraction of one-thousandth of a calorie.

In conclusion, it must be noted that the values of the peak heights (above background) in the case of a close sequence of transitions depends very markedly on the shape of the original peak, and particularly on the character of the sharp drop after the temperature  $T_c$ , which would probably be more gradual in the case of liquids. Consequently, the figure of 0.012 cal./g./ $^\circ\text{C.}$  estimated

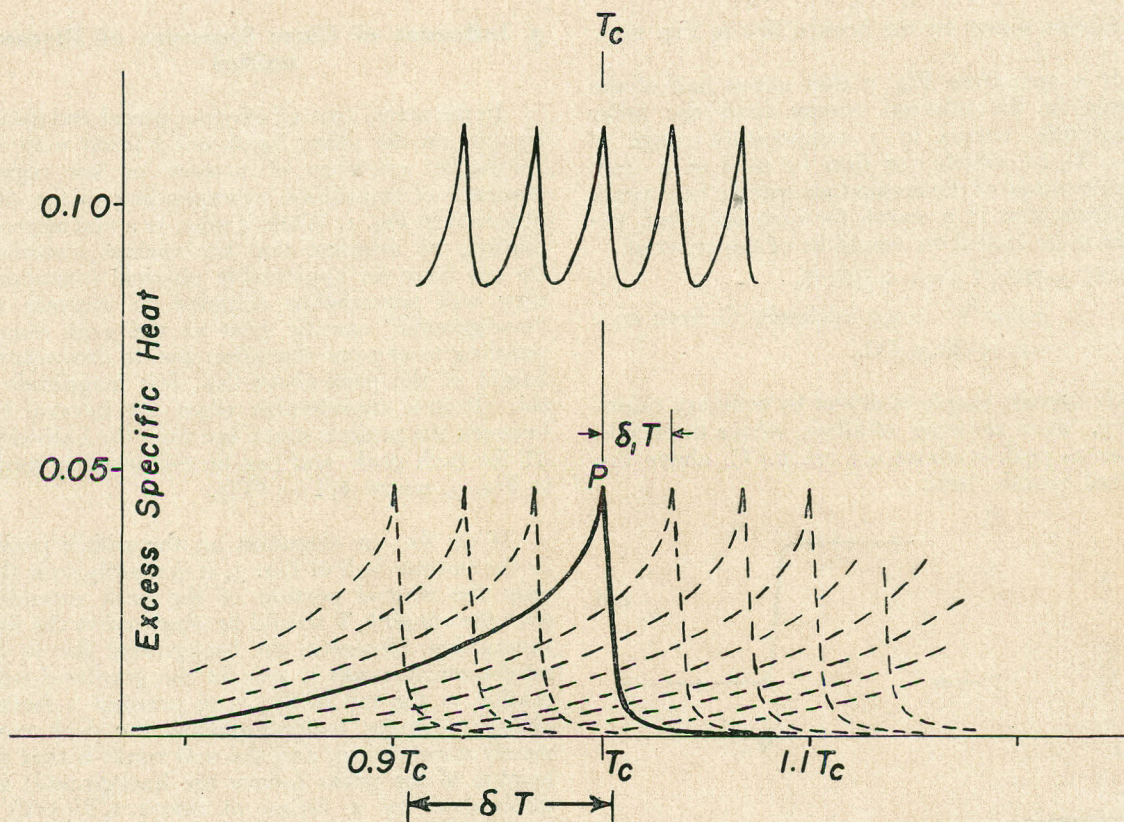


Fig. 3.—Diagrammatic representation of the smoothing and levelling effect of the consecutive series of energy jumps at intervals  $\delta_1 T = \delta T/3$ .

above could well require to be diminished several fold. Also, it is pertinent to mention that the anomalous viscosity increases observed well above the freezing point in tin and zinc have recently been interpreted<sup>7</sup> in terms of prefreezing cluster formation in the melts, giving an effective  $\Delta H$  of about 5 k cal./mole spread over 50°C.

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