PAKISTAN JOURNAL
OF
SCIENTIFIC AND INDUSTRIAL RESEARCH

Vol. 6, No. 4 October 1963

# POSSIBLE EXISTENCE OF DISCONTINUITIES IN THE FIRST AND HIGHER DERIVATIVES OF THE COEFFICIENT OF DILATATION OF PURE WATER

MAZHAR M. QURASHI

*Physics Division, Central Laboratories, Pakistan Council of Scientific and Industrial Research, Karachi*

(Received May 10, 1963)

In an effort to elucidate the nature and physical basis of the discontinuities observed in the activation energy $E_\eta$ for viscous flow of water (Qurashi and Ahsanullah, 1961) and dilute aqueous alcohol, a full differential analysis has been made of the accurate standard data on density of water from 0°C. to 40°C. The derivatives are first evaluated at 2°C. intervals, and the plot of the coefficient of dilatation, $\alpha = -(\Delta\rho/\Delta T)/\rho_0$, appears smooth but is not fitted by any simple function. The plot of $\Delta\alpha/\Delta T$ shows four inflections at 10°, 21°, 29° and 33°C., all of which temperatures agree within 1.5°C. with those of corresponding jumps found in the plot of $E_\eta/R$ from viscosity measurements.

Recalculation of $\alpha$ and $\Delta\alpha/\Delta T$ with $\Delta T = 1$°C. from 1°C. to 19°C. brings up two more steep drops in $\Delta\alpha/\Delta T$ at 5°C. and 8°C., (and probably one at 16°C.), while calculation of $\Delta^2\alpha/\Delta T^2$ with $\Delta T = 2$°C. indicates the likely presence of three smaller ones at 16°C., 18° C.and 37°C. The temperatures of all the nine jumps in $\Delta\alpha/\Delta T$ agree well with those of the nine jumps previously observed in $E_\eta/R$ in the range of 1°C. to 40°C. thus suggesting that the two phenomena have a common physical basis of inter-molecular aggregation or re-arrangement and are third order changes.

## 1. Introduction

A series of discrete jumps in the activation energy $E_\eta$ of viscous flow have recently been observed in some pure liquids and solutions through very accurate differential viscosity measurements on water by Qurashi and Ahsanullah,[1] on ethylene glycol by Ahsanullah and Qurashi,[2] and on aqueous alcohol by Ahsanullah, Ali and Qurashi.[3] In an effort to elucidate the nature and physical basis of these discontinuities, it was considered worthwhile to undertake an accurate investigation of the first and higher temperature-derivatives of other basic physical properties like refractive index and coefficient of dilatation. As previously pointed out,[1] the coefficient of dilatation (being essentially a bulk property) is one of the less sensitive of these properties, and therefore its study has been deferred until a fair measure of information had been obtained [1–3] on the measurements of $E_\eta = -R\,T^2 \Delta \ln \eta/\Delta T$.

Some preliminary attempts are currently being made in this laboratory to study directly through precision experiments the temperature variation of the coefficient of dilatation of ethylene glycol. On water, there already exist density measurements going up to the seventh decimal place in the range of 0°C. to 40°C. and the present communication presents a full differential analysis of this data. The International Critical Tables[4] (Vol. III) give the mean values for the two independent sets of determinations by (i) Chappuis and (ii) Thiessen *et al.* The individual values obtained by these two groups depart from the I.C.T. values by 2 units on the average in the *seventh* decimal place in the range of 0° to 18°C. and by about $2\frac{1}{2}$ units in the sixth decimal place from 20°C. to 40°C. However, this includes consistent as well as random errors, so that the precision of the measurements on a relative scale is expected to be considerably better (as shown by Qurashi,[5] for example in case of the viscosity of molten aluminium), so that we may fairly depend on accuracy of $\Delta\rho$ for 1° or 2°C. to the 7th place below 18°C. Above 20°C., accuracy to the sixth decimal place is assured, but it is further seen from the original data that the discrepancies between the groups show a systematic trend, with changes of only 2 to 4 units in the *seventh* decimal place per degree. Therefore, it is probable that values of $\Delta\rho$ for a 1° or 2°C. interval can be relied upon to this accuracy above 20°C.

## 2. The Coefficient of Dilatation and its First Derivative

For calculating the coefficient of dilatation, $\alpha = (\Delta V/\Delta T)/V_0 = -(\Delta\rho/\Delta T)/\rho_0$ as a function of temperature from the above data, it is first necessary to select a suitable thermal interval, $\Delta T$, consistent with the accuracy of the data and the fineness of the detail to be explored in $\alpha$ and $\delta\alpha/\delta T$. These two requirements are in effect contradictory, and an interval of 2°C. was selected as a suitable compromise in the first instance. It would yield an accuracy of approximately 1 to 2 parts per 1,000 in $\alpha$ over the range of 1°C. to 39°C.

Accordingly, the second column of Table 1 gives the values of $2\alpha \times 10^4$ as obtained from the differences between pairs of values of $\rho$ two degrees apart, $\rho_0$ being 0.9999. On the basis of the foregoing discussion, the third decimal place in this column will be subject to errors of the order of $\pm$ 1 to $\pm$ 3 units. These values of $\alpha$ are plotted as solid circles in the lower half of Fig. 1, and no discontinuities, nor even inflections are to be seen at first sight. However, the curve cannot be fitted accurately either by an exponential or by a cubic function, and this prompted the examination of the first derivative of the coefficient of dilatation i.e. $\delta\alpha/\delta T$.

TABLE 1.—VALUES OF $\alpha = -\frac{\Delta\rho}{\Delta T}\Big/\rho_0$ AND $\Delta\alpha/\Delta T$ AND $\Delta^2\alpha/\Delta T^2$ CALCULATED FROM THE STANDARD DENSITY DATA.

| Temperature T (°C.) | $2\alpha = -2\frac{\Delta\rho}{\Delta T}$ ($\times 10^4$) with $\Delta T = 2$ °C ($\rho_0 = 0{\cdot}9999$) | $4 \times 10^5 \times \frac{\Delta\alpha}{\Delta T}$ ($\Delta T = 2$ °C.) | $-4\frac{\Delta^2\alpha}{\Delta T_2 \Delta T_1} \times 10^5$ ($\Delta T_1 = 2$°C. $\Delta T_2 = 1$°C.) | $2\frac{\Delta\alpha}{\Delta T} \times 10^5$ ($\Delta T = 1$°C.) |
|---|---|---|---|---|
| 1.0 | —1.000 | — | | |
| | | | — | 3.45 |
| 2.0 | —0.655 | 6.79 | | |
| | | | 0.21 | 3.34 |
| 3.0 | —0.321 | 6.58 | | |
| | | | 0.18 | 3.24 |
| 4.0 | +0.003 | 6.40 | | |
| | | | 0.19 | 3.16 |
| 5.0 | +0.319 | 6.21 | | |
| | | | 0.21 | 3.05 |
| 6.0 | +0.624 | 6.00 | | |
| | | | 0.17 | 2.95 |
| 7.0 | 0.919 | 5.83 | | |
| | | | 0.17 | 2.88 |
| 8.0 | 1.207 | 5.66 | | |
| | | | 0.13 | 2.78 |
| 9.0 | 1.485 | 5.53 | | |
| | | | 0.08 | 2.75 |
| 10.0 | 1.760 | 5.45 | | |
| | | | 0.17 | 2.70 |
| 11.0 | 2.030 | 5.28 | | |
| | | | 0.23 | 2.58 |
| 12.0 | 2.288 | 5.05 | | |
| | | | 0.18 | 2.47 |
| 13.0 | 2.535 | 4.87 | | |
| | | | 0.11 | 2.40 |
| 14.0 | 2.775 | 4.76 | | |
| | | | 0.08 | 2.36 |
| 15.0 | 3.011 | 4.68 | | |
| | | | 0.10 | 2.32 |
| 16.0 | 3.243 | 4.58 | | |
| | | | 0.10 | 2.26 |
| 17.0 | 3.469 | 4.48 | | |
| | | | 0.08 | 2.22 |
| 18.0 | 3.691 | 4.40 | | |
| | | | 0.10 | 2.18 |
| 19.0 | 3.909 | 4.30 | | |
| | | | 0.09 | 2.12 |
| 20.0 | 4.121 | 4.21 | | |
| | | | 0.06 | 2.09 |
| 21.0 | 4.330 | 4.15 | | |
| | | | 0.08 | |
| 22.0 | 4.536 | 4.07 | | |
| | | | 0.08 | |
| 23.0 | 4.737 | 3.99 | | |
| | | | 0.08 | |
| 24.0 | 4.935 | 3.91 | | |
| | | | 0.08 | |
| 25.0 | 5.128 | 3.83 | | |
| | | | 0.06 | |
| 26.0 | 5.318 | 3.77 | | |
| | | | 0.09 | |
| 27.0 | 5.505 | 3.68 | | |
| | | | 0.06 | |
| 28.0 | 5.686 | 3.62 | | |
| | | | 0.05 | |
| 29.0 | 5.867 | 3.57 | | |
| | | | 0.10 | |
| 30.0 | 6.043 | 3.47 | | |
| | | | 0.06 | |
| 31.0 | 6.214 | 3.41 | | |
| | | | 0.04 | |
| 32.0 | 6.384 | 3.37 | | |
| | | | 0.07 | |
| 33.0 | 6.551 | 3.30 | | |
| | | | 0.09 | |
| 34.0 | 6.714 | 3.21 | | |
| | | | 0.06 | |
| 35.0 | 6.872 | 3.15 | | |
| | | | 0.04 | |
| 36.0 | 7.029 | 3.11 | | |
| | | | 0.07 | |
| 37.0 | 7.183 | 3.04 | | |
| | | | 0.06 | |
| 38.0 | 7.333 | 2.98 | | |
| 39.0 | 7.481 | — | | |

The third coulmn of Table I shows the values of 4 $(\Delta\alpha/\Delta T) \times 10^5$ calculated as the differences between pairs of values of 2 $\alpha$ separated by 2°C., while the fifth column gives 2 $(\Delta\alpha/\Delta T) \times 10^5$ evaluated upto 19°C. with $\Delta T = 1$°C. The third figure will in either case be uncertain by about 2 units on the basis of the experimental errors (as discussed above), which is represented by the radius of the hollow circles in Fig. I (top) giving the

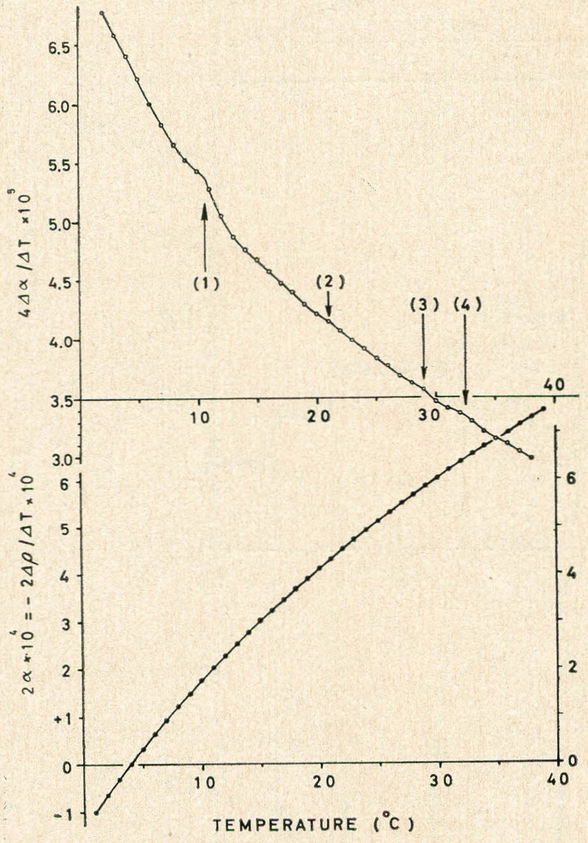


Fig. I.—Graphs of the coefficient of dilatation $\alpha = -\Delta\rho/\Delta T$ for water, shown as solid circles, and for $\Delta\alpha/\Delta T$ plotted as hollow circles, both calculated from the standard (I.C.T.) data for the density of pure water. The numbered arrows mark the positions of the four inflections observable in $\Delta\alpha/\Delta T$.

plot of 4 $(\Delta\alpha/\Delta T) \times 10^5$. This graph shows four, more or less clear, inflections marked by the vertical arrows, the largest ones at about 10°C. and 33°C. being quite unmistakable and considerably more than the probable experimental deviations. The shape of the graph is, moreover, generally reminiscent of that for $E\eta/R = -T^2\Delta \ln \eta/\Delta T$ obtained[1] from Bingham and Jackson's viscosity data[6] on water with $\Delta T = 2$ to 5°C. so that $d \ln \eta/dT$ appears to be comparable with $d\alpha/dT$. Also, the temperatures at the four inflections observable in $\Delta\alpha/\Delta T$ agree fairly well with those of the corresponding jumps in $E\eta/R$ found in our more accurate viscosity measurements [3] made with $\Delta T = 1$°C. and reproduced in the upper portion of Fig. 2.

Further support for this correspondence in detail is obtained by re-calculating both $\alpha$ and $\Delta\alpha/\Delta T$ with a finer thermal interval of 1°C., and then plotting $\Delta\alpha/\Delta T$ against temperature as shown in the inset to Fig. 2 (top). The similarity with the graph of $E\eta/R$ from viscosity measurements is particularly remarkable because $\Delta\alpha/\Delta T$ is only 1/1000 of $\Delta \ln \eta/\Delta T$. The horizontal portions (A to D) of constant $\Delta\alpha/\Delta T$ are clearly seen at 4.5°, 6.5° and 10°C. and also around 14°C., the four being separated by relatively steep jumps, as in the graph for $E\eta/R = T^2\Delta \ln \eta/\Delta T$. Thus, we can infer the existence of several discontinuous changes in $\delta\alpha/\delta T$; since this is the third derivative of the Gibbs function, the physical changes involved would (at most) be of the "third order".

## 3. Examination of the Second Differential of the Coefficient of Dilatation

Because the density data above 20°C. are less accurate, it is not feasible to use the small differential interval of 1°C. Nevertheless, in view of the foregoing indications, it was considered desirable to make an attempt to locate any remaining small inflections in the $\Delta\alpha/\Delta T$ curve above 20°C. by an alternative technique, viz. calculating the next derivative, $\Delta^2\alpha/\Delta T^2 = \Delta(\Delta\alpha/\Delta T_1)/\Delta T_2$, using $\Delta T_2 = 1$°C.

In the fourth column of Table I are given the values of $-4 \times \Delta(\Delta\alpha/\Delta T_1)/\Delta T_2 \times 10^5$ calculated with $\Delta T_1 = 2$°C., and $\Delta T_2 = 1$°C. These values are plotted as solid circles in the lower half of Fig. 2, while the crosses show some values obtained with $\Delta T_1 = \Delta T_2 = 1$°C. for the temperatures below 20°C. where the accuracy of the density measurements is known to be greater than at higher temperature. A smooth curve has been drawn through all these points, and the root-mean-square deviation of the plotted circles about the graph is $\pm$ 0.02 unit below 20°C., and nearly $\pm$ 0.03 from 20°C. to 40°C., which corresponds to 2 and 3 units, respectively, in the seventh decimal place in the original density measurements, and is about one-half of the expected magnitude of errors, thus confirming the validity of the arguments in section I regarding the probable precision of the values of $\Delta\rho$.

The inflections observed in the $(\Delta\alpha/\Delta T)$ curve of Fig. I (top) and the inset to Fig. 2

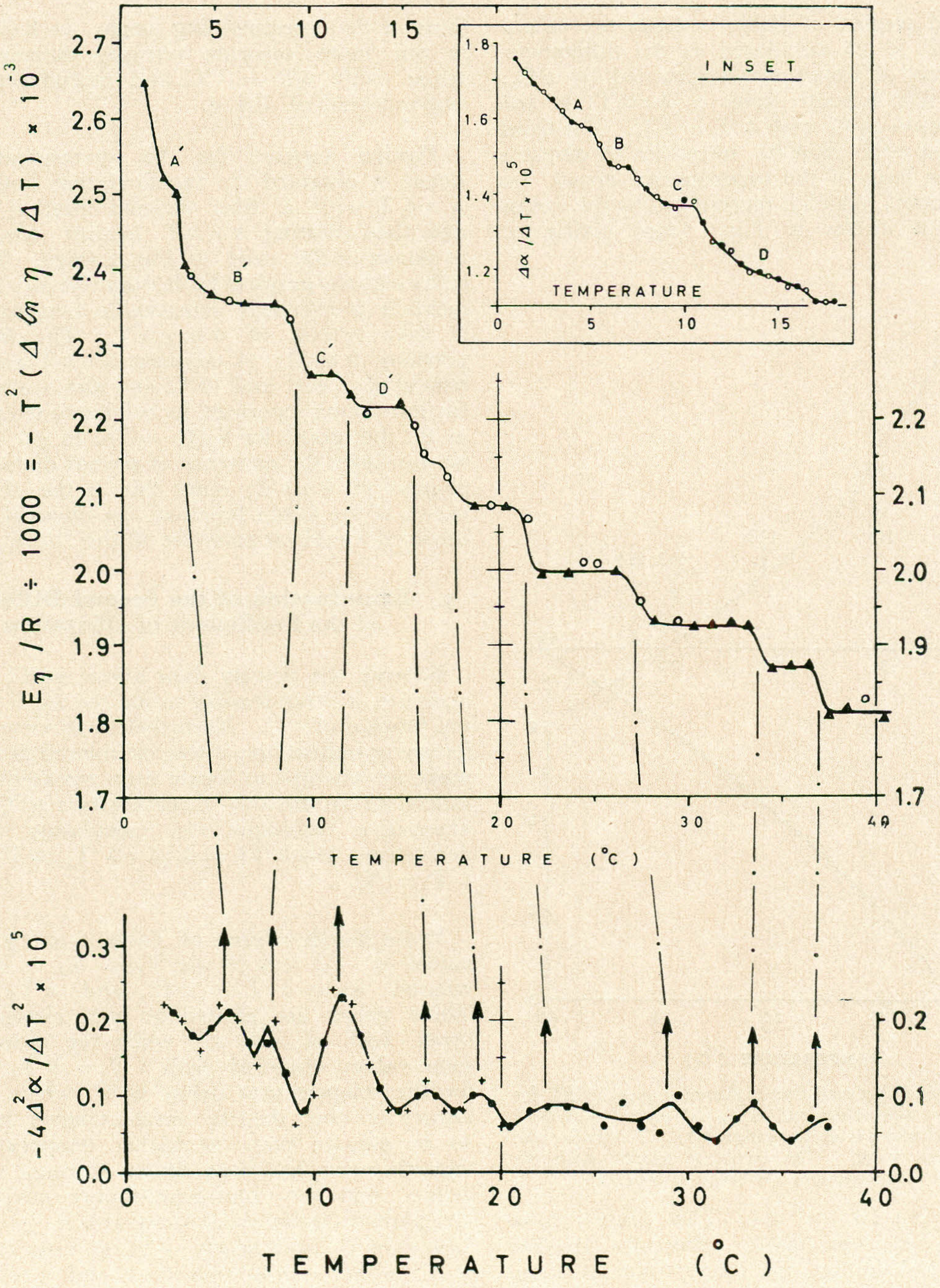


Fig. 2.—(top) Temperature variation of activation energy for the viscous flow of water measured as $E\eta = -T^2 \Delta \ln \eta / \Delta T$ with $\Delta T = 1$°C. The triangles are means of two separate experiments, the hollow circles being some of the individual readings that are too far apart for averaging. The standard deviations are represented approximately by the radius of the circles.

The inset shows the graph of $\Delta\alpha/\Delta T = -\Delta^2\rho/\Delta T^2$ calculated from 1°C. to 18°C., with $\Delta T = 1$°C. starting from the standard density data, first at the whole degrees (solid circles) and then at the half-degree (hollow circles). The best graph drawn through these points resembles that for $E\eta/R$, and shows three clear horizontal regions, A, B and C at 4.5°C. 6.5°C. and 10°C. and another less distinct one(D) from 13° to 15°C. These are to be compared with A,' B,' C,' D' marked on the graph $E\eta/R$.

Fig. 2.—(bottom) Graph of $-4\Delta^2\alpha/\Delta T^2$ calculated from 2°C. to 38°C. with $\Delta T_1 = 2$°C. for the first derivative and $\Delta T_2 = 1$°C. (plotted as solid circles). The peaks correspond to the sharp jumps in $\Delta\alpha/\Delta T$, and are to be compared with the jumps in $E\eta/R$ directly above. (The crosses show the points calculated with $\Delta T_1 = \Delta T_2 = 1$°C. from 1°C. to 20°C.)

(top) appear more clearly in the $\Delta^2 \alpha / \Delta T^2$ graph as sharp jumps; for example near 10°C. where the value of $4 \Delta^2 \alpha/\Delta T^2 \times 10^5$ goes up from a minimum of 0.08 to a peak of 0.23 within the space of 2°C. In addition to the six definite inflections found in Fig. 1 and the inset to Fig. 2 (top), three other probable ones are deducible from the lower half of Fig. 2 at temperatures of 16°, 18° and 36°C., respectively, giving a total of nine in the range of 4°C. to 40°C. The positions of the points of maximum slope in these inflections (i. e. max $\Delta^2 \alpha/\Delta T^2$) are marked by the short vertical arrows in Fig. 2. Direct comparison with the jumps in $E\eta/R$ in the top of Fig. 2 the marginal accuracy of the density data above 20°C.

However, it is to be noted that the largest discontinuity in one property does not correspond to the largest in the other property, so that it is quite possible that two or more types of inter-molecular rearrangements are involved in the various jumps, or that some of the jumps are incorrectly located due to marginal accuracy. It is hoped that further light will be thrown on this aspect of the problem by the results of measurements now in progress on the temperature variation of dilatation and refractive index for ethylene glycol, water and other simple liquids where $\alpha$ is more nearly uniform.

TABLE 2.—COMPARISON OF TEMPERATURES FOR SHARP JUMPS IN (i) E/R AND (ii) $\Delta\alpha/\Delta T$.

| No. of Discontinuity | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|
| Temperature from E/R | 3.0 | 9.5 | 11.8 | 15.6 | 17.5 | 21.6 | 27.3 | 33.9 | 36.9 |
| Temperature from $\Delta\alpha/\Delta T$ | 5.3 | 8.0 | 11.4 | 16.0 | 18.8 | 22.4 | 28.9 | 33.5 | 36.8 |
| Weighted Mean | 3.8 | 9.0 | 11.7 | 15.7 | 17.6 | 21.9 | 27.8 | 33.8 | 36.9 |
| | ∓0.8 | ±0.5 | ±0.1 | ∓0.1 | ∓0.1 | ∓0.3 | ∓0.5 | ±0.1 | ±0.0 |

shows a one-to-one correspondence between the two sets of phenomena.

## 4. Discussion

The degree of concordance between the temperatures at the sharp changes in $\Delta\alpha/\Delta T$ and those at jumps in $E\eta/R$ is brought out in Table 2, the last row of which gives the weighted means of pairs of corresponding temperatures, the viscosity data being given twice the weight of the other.

The root-mean-square deviation for the weighted mean temperatures at the various discontinuities is seen from Table 2 to be ± 0.4°C., while the average interval between successive discontinuities is about 4.1°C. It can therefore be fairly concluded that the two sets of discontinuities correspond fully with each other, i.e., the sharp variations of $\Delta \alpha/\Delta T$ and $\Delta \ln \eta/\Delta T$ correspond in detail, thus providing evidence for the physical reality of both these phenomena, despite

**Acknowledgement.**—The author is indebted to Prof. J. D. Bernal for discussion of the viscosity data and for suggesting examination of higher derivatives of other properties.

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