Kauzman(n)ia

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If old chemists never die, as the saying goes, but merely equilibrate, it should come as no surprise that an old chemical conundrum known as Kauzmann's paradox is now witnessing something of a renaissance after a long period of interment[1,2]. Two IISc scientists, Kishore and Shobha[3], are among a small band of researchers who have recently contributed to a revival of interest in Kauzmann and his eponymous paradox. The paradox refers to the behaviour of the entropy S of a supercooled liquid in the temperature regime below the glass transition temperature T_g; when S is extrapolated far enough through T_g, a temperature T_{k1} is reached at which S equals and ultimately falls below the entropy of the crystalline phase that is more stable at that temperature. As this would constitute an apparent failure of equilibrium thermodynamics, it is generally held that the glass transition always intervenes to forestall any such occurrence. The temperature T_{k1} thus represents the limit of absolute stability of the liquid

By the same token, a similar limit might also be expected to exist for a superheated solid. This expectation seems to be borne out by the work of Fecht and Johnson[4], who have identified a second Kauzmann temperature, T_{k2}, as the temperature at which the extrapolated entropy of a superheated solid becomes identical to that of the liquid.

The logical corollary has now been stated by Kishore and Shobha[3]: the temperature at which the extrapolated entropy of the superheated liquid coincides with the entropy of the vapour corresponds to a third (and presumably final) Kauzmann temperature, T_{k3}. Kishore and Shobha, using standard thermodynamics, together with considerable physical intuition, have determined T_{k3} for a series of simple substances; their results show a number of intriguing regularities

For instance, in many of the materials they have studied (including water and the alkali metals), T_{k3} is not very different from T_c, the critical temperature of that substance. Kishore and Shobha see this as evidence that the Kauzmann temperature is, in fact, nothing but the critical temperature. This could prove to be a very interesting connection, but its validity will certainly need to be tested further against data from other sources The more so because of the many uncontrolled approximations that are made in the calculation of T_{k3}, which is based on the following equation:

$$\Delta S^{v} = \int_{T_{k3}}^{T_b} C_p \, \mathrm{d} \ln T. \qquad (1)$$

Here, ΔS^{v} is the entropy of vapourization, C_p is the constant-pressure heat capacity and T_b is the boiling point of the liquid. The heat capacity, in turn, is given by the expression

$$C_p = a_1 + a_2 T + \frac{a_3}{T^2}, \qquad (2)$$

where a_1, a_2 and a_3 are temperature-independent constants. Among other approximations, C_p is determined from data that correspond to a pressure of 1 atm. At a critical point, the pressure obviously need not assume this convenient value, so it remains to be confirmed that the parameters a_1, a_2 and a_3 in eq (2) are not strongly pressure-dependent. The equivalence of T_{k3} to T_c, if true, would nicely complement the suspected equivalence between the ideal glass transition temperature and T_{k1}.

Another interesting result originates in a connection between the melting temperatures T_m of these and a few other substances and the Kauzmann temperatures T_{k1} and T_{k2}, which Kishore and Shobha are also able to calculate by their method. They find that T_m is approximately twice T_{k1} and approximately half T_{k2}, suggesting that

$$T_m = \sqrt{T_{k1} T_{k2}}. \qquad (3)$$

But errors of as much as 45% can be produced while using this result to predict T_m (as happens in the case of aluminium). However, if these errors are corrected by the simple expedient of introducing into eq. (3) a 'fudge factor' (different for each substance), so that T_m is now given by

$$T_m = \sqrt{\frac{T_{k1} T_{k2}}{n_m}}, \qquad (4)$$

then it turns out, quite remarkably, that the correction term n_m behaves exactly like the exponent β that describes stretched exponential dynamics in glassy materials and that characterizes their strength or fragility.

A measure of the propensity to form a glass also appears to reside in a quantity that Kishore and Shobha derive from their equations, which they refer to as the characteristic entropy constant. This quantity – apparently a constant for a given class of substances, such as the alkali metals – is directly proportional to the difference between T_m and T_{k1}. It is either the same as or is related to another measure of vitreous character proposed by Angell[5] that had, till now, little theoretical justification.

These examples of the many and varied ways in which the Kauzmann temperatures intrude into the physics and chemistry of bulk matter strongly suggest a fundamental structural role for them on par with other better-known characteristics of material behaviour. Their continued study – experimentally and theoretically – is sure to prove rewarding.

1. Kauzmann, W, *Chem. Rev*, 1948, **43**, 219
2. Cahn, R. W., *Nature*, 1995, **373**, 475.
3. Kishore, K. and Shobha, H K, *J. Chem Phys*, 1994, **101**, 7037
4 Fecht, H J and Johnson, W. L., *Nature*, 1988, **334**, 50.
5 Angell, C. A and Sichina, W., *Ann N Y Acad Sci*, 1976, **279**, 53.

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