

very realistic models of pores, $r_h = r/2$ where r is the capillary radius. For slit-type capillaries, $r_h = d$ where d is half the distance of separation between the plates; slit-type capillaries are a reasonable model for pores between plate-shaped minerals such as the aluminosilicates. The value of the coefficient in equation (2) was derived from measurements³ of the unfrozen water content as a function of temperature on several partially frozen, water-saturated, mineral-water mixtures, each differing quite considerably in their crystallographic structure and physico-chemical properties. These data for powdered basalt (a primary, basic rock), limonite-goethite (iron oxide) and kaolinite (an aluminosilicate mineral) are depicted in Fig. 1. The fitted curve is simply a plot of equation (2). We discuss elsewhere how deviations from this freezing law may arise in porous bodies as a result of differences in distribution of pore size, and how these may affect the calculated thickness of unfrozen water layers at temperatures near 0 °C. At lower temperatures, however, (−6 to −10 °C) when the thickness of the unfrozen water layer lies in the range of 5–8 Å, water-ice phase composition data for most mineral materials fall on the same temperature-thickness curve. Note that the similarity between these three different materials would not have been as apparent if instead of layer thickness, unfrozen water content was plotted as a function of θ using the more common units of g H₂O/g solid, because of differences in specific surface areas between the various materials.

We will further analyse the possible physicochemical basis for the freezing process. Our hypothesis may be elaborated as follows: In the force field caused by the forces emanating from the solid or resulting from surface curvature of the liquid in capillary pores, the chemical potential or the vapour pressure of the water is lowered compared with that of bulk pure water. The smaller the capillary and the thinner the layer of adsorbed water, the lower the water chemical potential. When freezing is initiated at 0 °C, only the water that has chemical potential equal to free water solidifies whereas water in narrow pores, or affected by the solid surface and therefore having lower potential, remains unfrozen. As the temperature of the system is lowered further, the chemical potential of water, in the form of ice, is correspondingly decreased⁴ creating a gradient that successively induces increments of the unfrozen water to solidify. Thus, two condensed phases of water can coexist at temperatures below 0 °C—that is, unfrozen liquid water and ice crystals. The unfrozen water can be present either in narrow capillaries or as thin adsorbed layers. At each temperature the chemical potential of the unfrozen water is equal to that of ice at this temperature, being in thermodynamic equilibrium and physical juxtaposition with the ice. The relationship of thickness of unfrozen water to temperature can therefore be viewed as dependent on (and also a measure of) the change in chemical potential of water with the radius of pores or the distance from the solid surface.

The mode of change in chemical potential of a capillary condensate with pore size is well established; the Kelvin equation is a special case applicable to cylindrical capillaries. In general, the chemical potential depends on the nature of the liquid (its molar volume and surface tension) and is independent of the nature of the solid composing the walls of the pores. For cylindrical and slit-type capillaries it is proportional to r_h^{-1} . For thin adsorbed layers it was shown for nitrogen^{6,7} and for water⁸, that adsorption data relating some measure of the chemical potential (vapour pressure) to the thickness of adsorbed layer for many solid adsorbents fall on a common curve termed by de-Boer and his associates⁶, the standard t curve. Thus the t curve seems to be characteristic of the adsorbate or adsorptive but virtually independent of the adsorbent. From these standard t curves it is also found that the chemical potential of the adsorbate usually varies with d^{-3} as expected for the classical van der Waals interaction resulting purely from dispersion forces acting between an atom and a slab⁹. Accordingly, and in view of the previous discussion on the mode of near-surface water freezing, we suggest that many porous bodies and adsorbents may have a common freezing curve relating the

layer thickness of unfrozen water or the hydraulic radius of pores containing them, to temperatures below 0 °C. Our data show that this is the case for a variety of minerals (Fig. 1). From the data of Mazur it seems also to be the case for biological systems.

One puzzling and unresolved finding is that the coefficient in equations (1) and (2) relating the temperature below freezing point to the hydraulic radius or the equilibrium thickness of water on the surface (or when converted to other units, relating the chemical potential to the distance from the surface) is smaller by a factor of five to ten than that predicted from the Kelvin equation. The tentative explanation of Mazur¹ that the contact angle of the water in the pores is not 0 ° but 80 ° does not seem to be sufficient in view of the fact that three different adsorbents are involved in deriving the relationship given in equation (2). Also, the fact that even at every close proximity to the solid the interaction still seems to vary with d^{-1} rather than with d^{-3} , is puzzling. Thus none of the presently known modes of interaction between solid porous adsorbent and liquid adsorbate seems to account completely and quantitatively for these experimentally determined generalised freezing relationships.

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Corrigenda

In the article "Evidence that mitogenic lectins induce changes in membrane fluidity" by R. E. Barnett, R. E. Scott, L. T. Furcht and J. H. Kersey (*Nature*, **249**, 465; 1974) the authors request that the following changes be made to the method. "The organisation of the membrane lipids was probed with a mixture of 3 spin labels, methyl 6-(4',4'-dimethyl-oxazolidinyl-N-oxyl)-heptadecanoate (10%), N-(1,1-dimethyl-2-hydroxyethyl)-6-(4',4'-dimethyl-oxazolidinyl-N-oxyl)heptadecamide (30%), and 1-[2-(1,1-dimethyl-2-hydroxyethylimino)cyclopentyl]-1-(4',4'-dimethyl-oxazolidinyl-N-oxyl)undecane (60%). The observed differences in the order parameter could also be caused by differential uptake or metabolism of the labels by the cells."

In the article "Role of f-gravity in cosmological models" by C. Sivaram, K. P. Sinha and E. A. Lord (*Nature*, **249**, 640; 1974) equation (2) should have read

$$\dot{R}^2 = \left(\frac{2}{3}\right)\pi G\rho R^2 + \left(\frac{2}{3}\right)\Lambda c^2 R^2$$

The Λ -term occurs with a positive sign, so that a minimum in the function $R(t)$ will occur only if the coupling constant G_T is negative (and Λ_T positive). Thus the conclusions of this paper are valid only if the coupling constant of strong gravity is taken to be negative. The authors wish to thank J. V. Narlikar for pointing this anomaly out to them.