

Vascular system of the giraffe

SIR—Both the discussions of the vascular system of the giraffe you have published recently mention venous valves, but both overlook the special 'seried' valves found at the entry of major tributaries into the axillary and brachial veins, though not into the jugular. Fewer occur in the closely-related okapi and some in the jugular and femoral veins of the bactrian camel¹.

These valves have a cusp proximal to the orifice of entry and another distal to it. Both are concave proximally. A number of slight differences occur in the arrangement of the cusps. Using fresh material from the camel the valve proved to be inefficient when pressure in main vein and tributary were very low, but when pressure in the main vein was raised progressively to as high as 200 mm of mercury regurgitation into the tributary was prevented. This pressure was higher than suggested for within the feet of the giraffe and surely for anywhere in the camel. The original workers had no access to fresh, unopened veins from a giraffe, but presumably their function in that animal would be the same and they would obviously be a great aid to the muscular pump. Why such valves should occur in the neck of the camel is hard to explain. The arterial structures in the neck of the camel² and both of the *Giraffidae*³ differ substantially.

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Small-particle physics and interstellar diamonds

SIR—Lewis *et al.*¹ have demonstrated the presence of extremely small (50 Å) diamonds in unshocked chondrite meteorites and have convincingly argued that these diamonds were formed in a circumstellar environment as metastable condensates. No consideration has yet been given to the possibility that diamond may be the stable condensate in this size regime and that thermodynamic predictions based on the bulk properties of minerals may not be applicable to nanometre-size particulates. Unfortunately, efforts to correct for the effects of the relatively large surface/volume ratio of particles in this regime are hampered by the lack of reliable data on the surface free energy of appropriate minerals.

Rietmeijer *et al.*² have argued that in the mineral system enstatite-tridymite-for-

sterite, for particle sizes ≤ 100 Å in diameter, the mineral mixture tridymite plus forsterite is more stable than enstatite alone, despite the fact that large enstatite grains are more stable than the mixture of large tridymite plus large forsterite grains. The reversal in the relative stability of the assemblage occurs because enstatite grains have a larger surface free energy than either forsterite or tridymite grains. I propose that a similar stability reversal could occur with carbon; for example, surface effects could make diamond the stable mineral phase for very small particles. Unfortunately, this hypothesis is difficult to test as values for the surface energy of both diamond and graphite are extremely unreliable. Bulk graphite is ~ 700 cal mol⁻¹ ($\sim 3 \times 10^{10}$ erg mol⁻¹) more stable than diamond³. The molar volume³ of graphite is 5.298 cm³ whereas that of diamond is 3.417 cm³. A reasonable estimate⁴ of the average surface free energy of a graphite sphere would be between 2,000 and 4,000 erg cm⁻²; diamond surface energies are in the range 3,700–9,800 erg cm⁻². Given the large uncertainty in the surface free energies for diamond and graphite it might be instructive to perform an alternative calculation to see if the hypothesis of a stability reversal appears reasonable for very small carbon particles.

If we assume a value for the surface free energy of graphite and also assume that particles smaller than 50 Å are more stable as diamond than as graphite, we can calculate the value of the surface free energy of diamond for which this set of assumptions would be correct. At equilibrium one mole of 50-Å diameter graphite grains would coexist with one mole of 50-Å diamond particles. But as the molar volume of graphite is larger than that of diamond this yields a surface area of 6.4×10^7 cm² for one mole of graphite grains while the surface area of a mole of 50-Å diamonds is 4.1×10^7 cm². We have therefore

$$(\text{area} \times \text{surface energy})_{\text{dia}} + \Delta G_{\text{dia}} = (\text{area} \times \text{surface energy})_{\text{gra}} \quad (1)$$

As ΔG_{dia} is $\sim 3 \times 10^{10}$ erg, if we assume that the surface energy of graphite is $\sim 4,000$ erg cm⁻², then the diamond surface energy for which equation (1) is correct is $\sim 5,500$ erg cm⁻². If the surface energy of graphite is only $\sim 2,000$ erg cm⁻² then the corresponding diamond surface energy is 2,400 erg cm⁻². In other words, because of the larger number of less dense graphite particles needed to contain one mole of carbon, diamond's surface free energy does not actually need to be smaller than that of graphite for diamond to be more stable and it can even be significantly larger. The consequences and implications of this hypothesis will be explored in another paper⁴.

Finally, it appears obvious that reliable

measurements or calculations of the surface free energies of solid particles are necessary if we ever hope to predict correctly the behaviour of very small particle systems. It should also be obvious that conventional 'thermodynamic wisdom' does not necessarily apply to nanometre-scale grains.

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Porosity of nuclear fuels

SIR—In interpreting Nichols' most interesting paper¹ on porosity in nuclear fuels, Robert Cahn² has slipped into the trap of considering mechanisms in isolation. He rightly comments on the importance of grain boundary porosity formation as a contributor to fission product gas release from nuclear fuels and the micrograph he shows, produced by Hyam and his co-workers in the UK Atomic Energy Authority Laboratories at Windscale, is one of several which formed the basis of the model³ still in use to predict such release. It is not correct, however, to deduce that fission product gas release in the columnar region is small. The high temperatures and thermal gradients that enable such grains to develop lead also to very high levels of gas release, probably by the bubble sweeping mechanism to which Nichols himself refers.

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How many Chernobyl fatalities?

SIR—Not to be stubborn, but for the sake of scientific truth, I would like to respond to J.H. Fremlin (*Nature* **327**, 376; 1987). The supralinear shape of the dose-response curve both for atomic worker's cancer and for cell depression in mice is not a hypothesis but an observed fact. It correlates additional effects with additional exposures, with the obvious conclusion that the background radiation will have corresponding effects, which appears to be born out by recent careful observations. Thus Fremlin's hypothesis that background radiation somehow immunizes people against further radiation is not born out by the facts.