Thus, the existence of 4 individual phases in a 1-component system is just about as improbable as a failing of the second law of thermodynamics. It is presumably even more improbable than a temporary deviation from maximum probability on a macro scale. I insist on calling it entirely improbable.

The problems encountered in the examples presented by Halliwell and Nyburg[1,4] (2-component system consisting of a gas phase, 2 liquid phases, and 2 solid phases) are identical with those presented here. Most probably, the two solids would occur in fixed proportions, and hence the system would be a normal 4-phase system.

I must stress that I do not discuss the probability of finding pairs of substances with the physical properties required to show 5 co-existing parts, as discussed by Halliwell and Nyburg. This problem certainly cannot be judged by 'normal probability theory'. The substances either exist, or they do not. If they exist, the system(s) in question would not have negative degrees of freedom.

J. BRYNESTAD

Advanced Teachers' College of
General and Educational Studies,
(Norges Lærerhøgskole),
Institute of Chemistry,
Trondheim, Norway.

[1] Halliwell, H. F., and Nyburg, S. C., *Nature*, **200**, 670 (1963).
[2] Brynestad, J., *Z. Phys. Chem.*, **36**, 356 (1963).
[3] Ricci, J. E., *The Phase Rule*, 4 (van Nostrand Co., 1951).
[4] Halliwell, H. F., and Nyburg, S. C., *J. Phys. Chem.*, **64**, 855 (1960).

THE first part of Brynestad's comments on our communication[1] is concerned with the 1-component system: two solids, liquid and vapour. We mentioned this in our original paper[2] only in passing, since we could not cite any example for discussion. Brynestad's comment raises an issue which we did not consider, namely, if such a system existed, whether the relative amounts of the two solid phases present would be in a fixed ratio. Brynestad, following Ricci[3], cites the case of d- and l-sodium chlorate. Before we turn to this interesting case, let us first examine Brynestad's analysis of a system which we did discuss in our original article, namely, a 2-component, five-phase system. We cited a number of 'near misses' such as the system mercury (m.p. − 38·9°) and diethylaniline (− 38·8°) and said that deuteration of the organic moiety in this and in other examples of 'near misses' could conceivably bring the triple points of the two components into exact coincidence. We interpreted Brynestad's original remarks[4] to mean that the chance of such a system existing was comparable to the chance of failure of the second law of thermodynamics. We see now that Brynestad did not mean this and that he does not rule out the possibility of such systems existing. He goes on to say that 'most probably the two solids would occur in fixed proportions'. We do not believe this to be correct for reasons given as follows. Moreover, Brynestad claims that the system would be 'a normal 4-phase system'. To say that solid mercury and solid diethylaniline are thermodynamically the same phase is to so alter the meaning of 'phase' as to derive it of any further value. One can easily trace the reasoning leading up to this conclusion: the phase rule is true; the mercury system + diethylaniline (for example) would, if considered to have five phases, imply a negative degree of freedom; negative degrees of freedom are not possible; therefore, at least two of the phases must be thermodynamically the same. To us it makes more sense to concede that negative degrees of freedom are possible; their existence is easily explained and the phase rule is not violated. We turn now to the system:

$$d\text{-NaClO}_3(c) + l\text{-NaClO}_3(c) + \text{melt} + \text{vapour}.$$
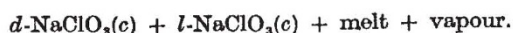
First we note that the phase rule is concerned with the number of phases present in equilibrium; it is not normally concerned with the masses of these phases or with the interfacial areas bounding them. However, in certain special cases the interfacial areas may be decisive for equilibrium. This is so in the sodium chlorate system at the triple point. If a crystalline solid is in contact with its melt, true equilibrium is reached only when the solid is a single crystal of shape (habit) which makes its surface-free energy a minimum. In the present case the system of lowest free energy is that of melt + vapour + a single crystal (of either d- or l-form) having the appropriate habit. There cannot be two or more crystals present since these, even if of the appropriate habit, will, on geometric grounds, have a total interfacial area larger than that of a single crystal of the same total mass (area ∝ mass$^{2/3}$). Of course, during the attainment of equilibrium we must keep the melt, vapour interface constant in area. We see then that for a system containing one appropriate crystal of d-NaClO$_3$ and one appropriate crystal of l-NaClO$_3$ the excess free energy of the system in terms of the masses of the crystals will be symmetric positive and not symmetric negative as assumed by Brynestad and by Ricci. (Perhaps it should be stressed that we are considering only those cases where the crystals do not touch each other but are each surrounded by at least several molecular layers of melt: relaxation of this condition would confuse the issue unnecessarily.) Thus this system in true equilibrium has three phases only and the question of a negative degree of freedom does not happen to arise.

We now turn back to the general case of systems containing two or more components the mutual miscibility of which brings their triple points into exact coincidence. We see that, because of surface-free energy effects, μ, the chemical potential (that is, free energy per unit mass) of a single crystal of given habit depends very slightly on its mass; the larger the mass the smaller μ. This means that the triple point is slightly affected by the mass of the crystal; again we assume no change in other interfacial boundaries. Strictly then, there will be equilibrium in an n-component $(2n + 1)$—phase system only if the n crystals (of appropriate habit) associated with the n melts have masses appropriate to the common triple point. This is different from saying, as does Brynestad, that the *ratios* of the masses of the solids are fixed: it is the actual masses which are important, for these govern the triple point.

H. F. HALLIWELL
Nuffield Foundation Science Teaching Project,
5–7 Tavistock Place,
London, W.C.1.

S. C. NYBURG

Department of Chemistry,
University of Keele.

[1] Halliwell, H. F., and Nyburg, S. C., *Nature*, **200**, 670 (1963).
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[4] Brynestad, J., *Z. Phys. Chem.*, **36**, 356 (1963).

Pressure-induced Gel – Sol Transition in Bentonite Suspensions

BY dilatometric measurements, Anderson, Leaming and Sposito[1] have recently shown that a reversible change in volume of about $2·4 \times 10^{-4}$ per cent occurs during the sol–gel–sol transition of a thixotropic sodium bentonite suspension. The volume increases during gelation and decreases during subsequent liquefaction. Since in a bentonite suspension neither crystallization nor dissolution accompanies the sol–gel–sol transition, the volume change is unexpected and has been attributed by the authors to an increased structure formation induced in the water by the bentonite gel structure. Previously, Anderson and Low have shown that the density of water is lower in the vicinity of the mineral particles of a bentonite suspension[2].

From the observed volume change one would expect that applying relatively high hydrostatic pressures should