

LETTERS TO THE EDITORS

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The Term 'Regular Solution'

IN 1920¹ I directed attention to the fact that the solubility of solids, plotted as a logarithm of mole fraction against reciprocal temperature, gives a family of curves in the case of solutions "where no molecular changes are involved". In 1927² I designated such solutions as 'regular' and in 1929³ I discussed the thermodynamic significance of this regularity, stating, in part: "From our picture of a regular solution as one in which orienting and chemical effects are absent, and in which the distribution and orientations are random, just as in an ideal solution, we may conclude that the probability of X_2 [species 2] is the same in the two solutions [ideal and actual] and, therefore, that the difference in entropy is zero. We cannot expect this conclusion to hold unless the random distribution of molecules persists. We may expect further that a small correction should be applied to take care of the change in entropy accompanying changes in volume, given by $(\partial S/\partial V)_T = (\partial P/\partial T)_V$; or we may state our principle in the following form. A regular solution is one involving no entropy change when a small amount of one of its components is transferred to it from an ideal solution of the same composition, the total volume remaining unchanged."

I referred to the possibility of expressing the partial molal enthalpy (of component 2) by the Margules series, $bx_1^2 + cx_1^3 \dots$, but showed that the behaviour of many solutions can be adequately expressed by the first term alone. It became evident, soon after⁴, that the mole fraction should be replaced by the volume fraction, and the coefficient b was evaluated in terms of the pure components.

The term 'regular solution' has now come into general use, but not always in conformity with the above definition. For example, Guggenheim⁵ uses it as follows: "We now turn to a class of mixtures called *regular mixtures* or *regular solutions* defined by the properties $\log f_1 = wx^2/RT$ —wherein w is not merely independent of the composition but independent of the temperature.—The name *regular solution* was first used by Hildebrand." Rushbrooke⁶ writes a certain partition function and says, "A solution for which the partition function is given by equation (8) is known as a *regular solution*". Longuet-Higgins⁷ states, "This theory [of regular solutions] assumes that in a liquid mixture (a) the molecules are arranged in a regular lattice, (b) that the separate liquid components have ordered structures of the same type and (c) that the intermolecular potential energy is the sum of contributions from nearest neighbours in the lattice, the contribution of two neighbouring molecules depending only on their chemical nature".

I cite these differences not for the purpose of asserting my rights as the inventor of the term but to urge that so useful a concept, to which a simple definite meaning was originally attached, should not be robbed of its significance by different writers re-defining it each in his own way. I have no objection to a re-definition that may appear desirable in the light of present knowledge; but it should be made by general consent.

One question does arise in connexion with the original definition, wherein ideal entropy and random distribution of molecules were regarded as equivalent. We have since learned from a succession of investigators, culminating with Flory and Huggins⁸, that the entropy of mixing molecular species of significantly different size, even though randomly mixed, is not the ideal entropy; therefore, we should decide whether to attach the term 'regular solution' to one or the other of these concepts. Prof. Scott and I, in our "Solubility of Nonelectrolytes" (third edition), have used it to mean ideal entropy, for example, the partial molal entropy of transfer $\bar{s}_1 - s_1^0$ from pure liquid to solution of mole fraction x_1 is $\bar{s}_1 - s_1^0 = -R \ln x_1$. This is more restricted than the other definition, but except for solutions of high polymers, it holds well enough for many purposes and permits expressing the activity coefficient in terms of the enthalpy. The Flory-Huggins equation involves certain assumptions that prevent it from being regarded as an accurate expression of the concept of complete randomness. To define the regular solution in terms of ideal entropy better fulfils the function of a useful reference state, well explained by Scatchard⁹: "... The student should be taught that thermodynamics deals with differences, that the number of differences to be considered can be reduced greatly by the use of reference states, that the magnitude of the differences can be reduced by the use of deviation functions, and that the choice of reference states and of deviation functions is entirely a matter of convenience, which should not be allowed to reduce the accuracy of any calculation ...".

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¹ *J. Amer. Chem. Soc.*, **42**, 2180 (1920); **43**, 2172 (1921).

² *Proc. U.S. Nat. Acad. Sci.*, **13**, 267 (1927).

³ *J. Amer. Chem. Soc.*, **51**, 66 (1929).

⁴ Scatchard, G., *Chem. Rev.*, **8**, 321 (1931). Hildebrand, J. H., and Wood, S. E., *J. Chem. Phys.*, **1**, 817 (1933).

⁵ Guggenheim, E. A., "Thermodynamics" (North-Holland Pub. Co., Amsterdam, 1949).

⁶ Rushbrooke, C. S., "Introduction to Statistical Mechanics" (Clarendon Press, Oxford, 1949).

⁷ Longuet-Higgins, H. C., *Proc. Roy. Soc.*, **A**, **205**, 247 (1951).

⁸ For ref., see Hildebrand, J. H., *J. Chem. Phys.*, **15**, 225 (1947).

⁹ *J. Chem. Educ.*, **27**, 291 (1950).

Change of Resistivity of Gold by Cold-working at Liquid-Air Temperature and its Recovery by Temporary Heating

SOME time ago Molenaar and Aarts¹ observed that the increase of the resistivity of copper, silver and aluminium wires, caused by a plastic deformation at liquid-air temperature, decreased on keeping the wires at room temperature. The recovery of the resistivity was not accompanied by a recovery of the mechanical properties. The stress-strain curve at liquid-air temperature was not changed by this temporary heating.

We have now measured the recovery of the resistivity of gold wires. A gold wire, which had been soft-annealed, was stretched approximately 7 per cent at liquid-air temperature and its resistance measured. This elongation caused a relative increase of the resistivity of about 1.5 per cent. The wire was then warmed up to different temperatures, at