

Hume-Rothery's 15% size rule for the solid solubility of metallic phases.^{119,120} Hume-Rothery's empirical size rule states that if two substances differ in size by more than $\pm 15\%$, very limited solid solubility is to be expected; but if they differ by less than 15% , then solid solubility is expected if other factors are favorable.^{119,120} Waber *et al.*⁵ have shown, considering only the size factor, that for 619 binary alloy systems where the size difference is greater than $\pm 15\%$, 90% of these systems exhibited very limited solid solubilities, and for 804 systems where the size difference is less than $\pm 15\%$, only 50% of these systems exhibited extensive solid solutions. This is a very striking confirmation of Hume-Rothery's size rule, proposed almost 30 years ago.

Eshelby noted that the size factor, S.F., is given by

$$\text{S.F.} = \left[\left(\frac{RT_m}{\mu V} \right) \left(\frac{1 - \sigma}{1 + \sigma} \right) \right]^{\frac{1}{3}}, \quad (29.1)$$

where R is the gas constant, T_m is the melting point, μ is the shear modulus, V is the atomic volume, and σ is Poisson's ratio. It should be noted that the term $RT_m/\mu V$ is the Leibfried number, L , which was discussed in Section 26. Since $L \approx 0.030$ and $(1 - \sigma)/(1 + \sigma) \approx 0.5$ (Section 23), we find $\text{S.F.} \approx 0.13$ or 13% . Eshelby explained that if the size difference, $|r_A - r_B/r_A| = \epsilon$, is smaller than the size factor calculated for the solvent, A , no solid miscibility gap is expected; but if ϵ is greater than the size factor, then the formation of two phases, i.e., limited solid solubility, is expected.

As mentioned in Section 26, it was thought that the modified Leibfried number, L' , was more accurate than L , and accordingly L' was used in calculating the size factor. Furthermore, it was mentioned in Section 26 that $L' \approx \mathcal{G}$, where \mathcal{G} is the Bragg number, and therefore a second set of size factors was calculated by using \mathcal{G} instead of L' . The size factors calculated from L' and \mathcal{G} (Table XXII) and the term $(1 - \sigma)/(1 + \sigma)$ (Table XX) are listed in Table XXV. From these two, L' and \mathcal{G} , a size factor, called the "best value," was chosen, which is also given in Table XXV. This best value is thought to represent the best size factor for a given element as calculated by Eshelby's method.

Friedel's Approach. Friedel independently suggested another method for determining the size factor for each element.¹²¹ He gave the following

¹¹⁹ W. Hume-Rothery, G. W. Mabbott, and K. M. Channel-Evans, *Phil. Trans. Roy. Soc. London* **A223**, 1 (1934).

¹²⁰ W. Hume-Rothery, "Structure of Metals and Alloys," 1st ed. (1939); and W. Hume-Rothery and G. V. Raynor, *ibid.*, 3rd ed. Inst. Metals, London, 1954.

¹²¹ J. Friedel, *Advan. Phys.* **3**, 504 (1954).

expression:

$$\text{S.F.} = \left[\frac{RT_m \chi}{\pi r^3 N} \right]^{\frac{1}{3}} = \left[\frac{4RT_m \chi}{3V} \right]^{\frac{1}{3}}, \quad (29.2)$$

where χ is the compressibility and r is the atomic radius. Since it has been shown that Richard's rule is a poor approximation, the constant K was substituted for R in Eq. (29.2) (see Section 27). The value of the constant K depends on the crystal structure of the element just prior to melting. The size factor determined in this manner is also shown in Table XXV, under the column heading "Calculated from Friedel's approach."

Discussion. The values determined from the two approaches were then averaged (except for a few elements) to give the final value, which is believed to best represent the size factor for a given element. If the size factors differed by more than ± 6.00 from one another, the two values were not averaged but the lower value of the two was chosen to be the representative value for that particular element. This lower value was chosen for graphite, diamond, white and red phosphorus, manganese, selenium, and thallium. Since there was only one value for black phosphorus, it necessarily was used.

The mean value for the size factor based on L' is 12.97 ± 2.49 ; based on \mathcal{G} it is 12.71 ± 2.58 ; based on the best value from Eshelby's approach it is 12.50 ± 2.48 ; and based on Friedel's approach it is 13.92 ± 3.63 . The mean value of the final best representative values is 12.88 ± 2.73 . The error for the final best representative value ± 2.73 corresponds to a percentage error of ± 21.2 , which is quite good. The final best representative value varies from a minimum of 7.81 for gallium to a maximum of 50.56 for graphite. These values for the elements are shown in Fig. 34. The dependence on the location of the element in the Periodic Table is again evident. The large values for the alkali and alkaline-earth metals decrease slowly as one moves across each period, reach a minimum near iron and its congeners, increase to a maximum at the group IB elements, decrease to a minimum near the group IIB elements, and finally attain a maximum near the group VB elements.

The size factors for the rare earths show a steady increase with increasing atomic number (Fig. 33b). The large values for europium and ytterbium correspond to the large values of the alkaline-earth metals; again this shows the divalent nature of these two rare-earth metals.¹³ The value for α -Ce is included for comparative purposes; this value, because of its higher valence, would not necessarily be expected to lie on the same curve with the other rare earths.

Preliminary results from an extension of the study of the prediction of solid solubility in metallic alloys⁸ indicated that a slight improvement could be gained by using the individual size factors from Eshelby's approach