

Generalizing the Phase Rule

William B. Jensen

Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221-0172; jensenwb@email.uc.edu

The purpose of this short note is to briefly summarize four points intended to supplement the recent article by Alper on the Gibbs phase rule (1).

First. All of the examples discussed by Alper may be elegantly incorporated within the phase rule by replacing the conventional form of the rule,

$$f = c + 2 - p \quad (1)$$

with an expanded form,

$$f = (s + 2) - (p + e + r) \quad (2)$$

in which s stands for the number of chemical species (or constituents, in Alper's terminology), e is the number of independent equilibrated chemical reactions involving these species, r is the number of additional independent stoichiometric restraints interrelating their concentrations or activities beyond the requirement that the mole fractions in each phase must sum to 1, and p is, of course, the number of phases. Most of the examples discussed by Alper involve the temperature and pressure dependency of p , e , and r in the above expression.

Equation 2 has obviously been obtained by replacing the number of components (c) in the conventional form of the phase rule with the expression

$$c = s - e - r \quad (3)$$

This expansion was apparently first suggested by Wind in 1899 (2). Since then it has been repeatedly proposed in the literature with minor variations, starting with Richards in 1916 (3) and again with De Donder in 1920 (4), Jouguet in 1921 (5), Van Rysselberghe in 1932 (6), Bowden in 1938 (7), and Franzen in 1986 (8). It has appeared in several books on the phase rule and on thermodynamics in general (9–14), the most thorough discussion being that given by de Heer in his 1986 monograph (15). Since then, an increasing number of physical chemistry textbooks have also contained discussions of the expanded rule, including several of those referenced by Alper.

Second. Setting the value of the number of thermodynamic intensities or field variables (v) at a value of 2 (i.e., for temperature and pressure alone), as is done in the conventional formulation, actually represents a special case of the rule. A truly general statement of the phase rule requires that this parameter be left as a variable whose value is to be assigned according to the nature of the system being described (3, 16, 21, 22). Thus the fully generalized form of equation 2 should be written as

$$f = (s + v) - (p + e + r) \quad (4)$$

This is not only necessitated by relatively esoteric systems in which the state of the system is sensitive to magnetic or electric fields, for example, but also occurs in more common situations. Thus introductory textbooks on ceramics (17), metallurgy (18), materials science (19), and geochemistry (20) all make use

of the so-called reduced, condensed, or "isobaric" phase rule:

$$f = (s + 1) - (p + e + r) \quad (5)$$

in which the number of field variables has been reduced from 2 to 1 (temperature only) owing to the absence of volatile species in most of the phase diagrams of interest in these fields. Expansion of the number of variables from 2 to 3 occurs in the fields of colloid chemistry and surface chemistry owing to the increased importance of surface tension as a variable (21–23)

$$f = (s + 3) - (p + e + r) \quad (6)$$

and Bikerman has discussed the case of the variation of the vapor pressure of small bubbles of liquids with size from the same standpoint, using the curvature of the bubble as the third variable (24).

Third. There has long been a debate about whether the phase rule needs to be even further modified when dealing with systems involving optical enantiomers (25). Opinion on this issue remains divided. Scott (26) and Wheeler (27) have both proposed modifications, whereas others seem to feel that they are unnecessary (28).

Fourth. There is a pedagogical issue involved in the continued preoccupation with having students do problems in which they are expected to assign the number of phases and components ahead of time in order to calculate or predict the degrees of freedom for the system. As pointed out by Ricci almost 50 years ago (28), and more recently by Bent and Bent (29), this is really a case of putting the cart before the horse, since in actual applications of the phase rule one experimentally determines f and p and then proceeds to calculate c , rather than the other way around. Ricci was not particularly impressed with the expanded phase rule, arguing that it merely transferred the problem of determining the number of independent compositional variables from the component term (c) to the equilibrated reaction term (e). Richards, on the other hand, argued that this was precisely its virtue (3), since it is really the value of e rather than c that one is attempting to calculate from experiment, or, in the words of Bent and Bent, the number of "active tendencies" versus the number of "passive resistances" present in the system.

Literature Cited

- Alper, J. S. *J. Chem. Educ.* **1999**, *76*, 1567–1569.
- Wind, C. H. *Z. physik. Chem.* **1899**, *31*, 390–397.
- Richards, T. W. *J. Am. Chem. Soc.* **1916**, *33*, 983–989.
- De Donder, T. *Leçons de thermodynamique et de chimie physique*; Gauthier-Villars: Paris, 1920; pp 125–139.
- Jouguet, E. *J. Ecole Polytech.* **1921**, *21*, 61–181.
- Van Rysselberghe, P. *J. Phys. Chem.* **1932**, *36*, 1733–1737.
- Bowden, S. T. *Nature* **1938**, *141*, 331.
- Franzen, H. F. *J. Chem. Educ.* **1986**, *63*, 948–949.
- Bowden, S. T. *The Phase Rule and Phase Reactions*; Macmillan: London, 1938; pp 287–290.

10. De Donder, T.; Van Rysselberghe, P. *Thermodynamic Theory of Affinity, A Book of Principles*; Stanford University Press: Stanford, CA, 1936; pp 68–71.
11. Prigogine, I.; Defay, R. *Chemical Thermodynamics*; Longman: London, 1954; Chapter 13.
12. Denbigh, K. *The Principles of Chemical Equilibrium*; Cambridge University Press: Cambridge, 1955; pp 185–186.
13. Zernike, J. *Chemical Phase Theory*; Kluwer: Deventer, Netherlands, 1955; Chapter 1.
14. Everdell, M. H. *Introduction to Chemical Thermodynamics*; Norton: New York, 1965; pp 306–312.
15. de Heer, J. *Phenomenological Thermodynamics with Applications to Chemistry*; Prentice Hall: Englewood Cliffs, NJ, 1986; Chapter 21.
16. Reisman, A. *Phase Equilibria*; Academic: New York, 1970; p 7.
17. Norton, F. H. *Elements of Ceramics*; Addison-Wesley: Cambridge, MA, 1952; p 117.
18. Hume-Rothery, W.; Christian, J. W.; Person, W. B. *Metallurgical Equilibrium Diagrams*; Institute of Physics: London, 1952; p 26.
19. Brophy, J. H.; Rose, R. M.; Wulff, J. *The Structure and Properties of Materials*, Vol. 2; Wiley: New York, 1966; p 39.
20. Gill, R. *Chemical Fundamentals of Geology*; Hyman: London, 1989; p 39.
21. Tolman, R. C. *J. Am. Chem. Soc.* **1913**, *35*, 307–317.
22. Tolman, R. C. *J. Am. Chem. Soc.* **1913**, *35*, 317–333.
23. Ross, S.; Oliver, J. P. *On Physical Adsorption*; Interscience: New York, 1964; pp 1–5.
24. Bikerman, J. J. *Physical Surfaces*; Academic: New York, 1970; pp 57–61.
25. van't Hoff, J. H. *Chem. Ber.* **1902**, *35*, 4252–4264.
26. Scott, R. L. *J. Chem. Soc., Faraday Trans.* **1977**, *73* (11), 356–360.
27. Wheeler, J. C. *J. Chem. Phys.* **1980**, *73*, 5771–5777.
28. Ricci, J. E. *The Phase Rule and Heterogeneous Equilibria*; Van Nostrand: New York, 1951; Chapter 1 and pp 164–168.
29. Bent, H. A.; Bent, B. E. *J. Chem. Educ.* **1987**, *64*, 249–251.