

**Thermodynamics of Natural Systems, Second Edition**  
by G.M. Anderson

**Changes and Corrections**

- p. 319** “The number of variables (system properties) that must be fixed in order to fix all system properties is known as the system variance or degrees of freedom.”

Because the term “system” can mean a specific composition (e.g., a 1.2 molal solution of NaCl in water) or a possible range of compositions (e.g., the system C-O-S-H), the statement above might prove confusing. The best remedy is to remember that the derivation of the phase rule is based on the Gibbs-Duhem equation, one equation for *each phase*. Therefore “system properties” refers to the properties of the phases in the system, not the properties of the system as a whole, which, if it was of any interest, would be the weighted average of the phase properties. So, for example, for  $c = 2; p = 1, f = 3$ , and the usual choices are  $T, P$  and an exact composition such as “1.2 molal NaCl”. But for  $c = 2; p = 2, f = 2$ , and a choice of  $T$  and  $P$  in a two-phase field will fix the properties of both phases, whatever the composition within that field, but does not fix the properties of the system as a whole because the proportions of the phases can vary.

- p. 320** The second paragraph begins:

“Degrees of freedom can also be described as the number of intensive variables that can be changed (within limits) without changing the number of phases in a system.”

This statement is true in some cases, but not all. A discussion of which cases are which is not very useful, so it is better to just forget this sentence.

- p. 386** The  $h^\circ$  and  $s^\circ$  terms in the equation preceding (13.42) should be  $h_0^\circ$  and  $s_0^\circ$ .

- p. 408** In equation (14.10)  $xi$  should be  $x_i$ ,

$$\Delta_{mix}S_{ideal\ sol'n} = -3R \sum_i x_i \ln x_i$$

- p. 412** 7 lines from bottom: 263.32 should be 268.32.

**Note: The corrections below have been made in the second printing of the text, along with a few other minor changes.**

- p. 20** Two lines above §2.5.1: formula, not formulas. Same typo in the header for §6.5.2, p. 174. Also on pp. 269 and 271. This appears to be a typo introduced by CUP and may turn up in other places as well.

- p. 79** In item 2 in the middle of the page, it says that “In these cases a second form of work (non- $PV$  work) is being done.” This might better read “In these cases a second form of work (non- $PV$  work) is *capable* of being done.” An energy difference (such as  $P\Delta V$  or  $-\mathcal{A} d\xi$ ) might or might not be used to do work. This is expanded upon in §8 of the file “Additional Material” on the Cambridge U.P. web site.
- p. 90** 6 lines from bottom: It is more accurate to say “net heat” rather than “total heat” here, because in the cycle heat is input along the top (high  $T$ ) isotherm and output along the bottom (low  $T$ ) isotherm.
- p. 96** 9 lines from bottom: “our conclusion in §4.10” should read “our conclusion in §4.12.1”.
- p. 102** 11 lines from bottom: “discussed in §C.4” should be “discussed in §C.2.4”.
- p. 117** Figure 5.3.  $\Delta H_3$  should actually be  $\Delta H_2 - \Delta H_1$  rather than  $\Delta H_1 - \Delta H_2$ , in order that  $\Delta H_3$  (for the reaction  $A + B \rightarrow AB$ ) be negative, that is, exothermic.
- p. 142** Equation 5.33: A plus sign (+) is missing between  $S_{T_r,i}^\circ(T - T_r)$  and  $a_i$ .
- p. 145** In equation (5.41) the subscripts on the right side are interchanged. It should read

$$\begin{aligned}\Delta S &= S_{P_2} - S_{P_1} \\ &= R \ln \frac{P_1}{P_2}\end{aligned}\quad (5.41)$$

- p. 194** The subscript on  $x$  in equation (7.31) should just be 1, not  $x_1$ .

$$\begin{aligned}\mu_1 - G_1^\circ &= nRT \ln x_1 \\ &= RT \ln x_1^n\end{aligned}\quad (7.31)$$

- p. 285** 6 lines from bottom: Omit right parenthesis after the word *functionally*.
- p. 300** The  $T^2$  coefficient in equation (10.80) should be 0.161221, not 0.0161221. Therefore the coefficient for the  $T$  term in the top equation on p. 301 should be 0.322442, not 0.0322442. In the following equation on p. 301,  $(T/1000)^2$  in the final term should be  $(T/1000)$ .
- p. 310** Second line in §10.7: one-parameter, not two-suffix.
- p. 319** The statement in the footnote is incorrect. Additional forms of work result in additional independent variables, not in additional degrees of freedom. This is discussed in §3.2 in the “Additional Materials” file on the CUP web site.
- p. 352** In Figure 12.5, the numbers on the  $x$ -axis from 0.025 to 1.075 should be positive, not negative as shown.

- p. 374** The units of the values of the van der Waals parameters  $a$  and  $b$  in the box were omitted. These parameters are calculated using equations (13.19) and (13.20) with  $T_c$  in Kelvins and  $P_c$  in bars, but the value of the gas constant  $R$  used is  $83.1451 \text{ cm}^3 \text{ bar K}^{-1} \text{ mol}^{-2}$ . The units of  $a$  are thus  $\text{cm}^6 \text{ bar mol}^{-2}$ , and of  $b$  are  $\text{cm}^3 \text{ mol}^{-1}$ . These parameters are often reported in units of  $\text{J m}^3 \text{ mol}^{-2}$  and  $\text{m}^3 \text{ mol}^{-1}$ , respectively, where

$$\begin{aligned} \text{J m}^3 \text{ mol}^{-2} &= \text{cm}^3 \text{ bar K}^{-1} \text{ mol}^{-1} \times 10^{-7}, \quad \text{and} \\ \text{m}^3 \text{ mol}^{-1} &= \text{cm}^3 \text{ mol}^{-1} \times 10^{-6} \end{aligned}$$

- p. 410** 6 lines from bottom: Sentence should read “These calculations are illustrated on page 412 and Figure 14.4”.  
4 lines from bottom: “cell”, not “call”.
- p. 474** 5 lines from bottom: (16.1), not (10.1).
- p. 524** 7 lines from top: “. . . all three phases.” not “. . . all three break phases.”
- p. 539** 7 lines from bottom: Figure 17.23 should be Figure 17.22.
- p. 563** 7 lines from bottom: The sentence reads “In a closed system, we cannot change the chemical potentials of components  $\text{N}_2$  and  $\text{H}_2$ , . . .”. This is true (at constant  $T$  and  $P$ ), but the sentence would read a little easier by substituting “amounts (or mole numbers)” for “chemical potentials”. This substitution should also be made in the following sentence (“However, the chemical potentials of the species. . .”).
- p. 565** Top. Here affinity is equated with the vector  $A \rightarrow A'$ , the “distance” between products and reactants. As you can see from equation (18.59), affinity is actually the rate of change of  $\mathbf{G}$  with respect to  $\xi$ , the slope of the curve in Figure 18.8. What I meant to say was that it is the affinity term,  $-\mathcal{A} d\xi$ , or more exactly the integral of this term, that is the distance in joules between products and reactants. I say it better on p. 85, line 4.
- p. 581** The molar volume of muscovite is  $140.87 \text{ cm}^3 \text{ mol}^{-1}$ , not 14.087.
- pp. 583, 584** Column headings have unaccountably been omitted here. They are the same as on previous pages.
- p. 620** Last sentence in §G.1: “between” should be “because”.  
The work of Schottky et al. (1929) discussed in Appendix G is not quite as obscure as I suggested. Both Froese (1981) and Prigogine and Defay (1954) refer to it.
- Froese, E., 1981, Applications of thermodynamics in the study of mineral deposits. Geological Survey of Canada, Paper 80-28, 38 pp.
- Prigogine, I., and Defay, R., 1954, Chemical Thermodynamics: London, Longmans Green, 543 pp.

- p. 635** Missing from References:  
Millero, F.J., 1996, *Chemical Oceanography*, 2nd ed. CRC Press, Boca Raton, Florida.
- p. 638** Missing from References:  
Robie, R.A., Hemingway, B.S., and Wilson, W.H., 1976, The heat capacities of Calorimetry Conference copper, muscovite  $\text{KAlSi}_2(\text{AlSi}_3)\text{O}_{10}(\text{OH})_2$ , pyrophyllite  $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$ , and illite  $\text{K}_2(\text{Al}_7\text{Mg})(\text{Si}_{14}\text{Al}_2)\text{O}_{40}(\text{OH})_8$  between 15 and 375 K, and their standard entropies at 298.15 K. U.S. Geological Survey Jour. Research v.4, pp. 631–644.