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Thermodynamics of Natural Systems, Second Edition

by G.M. Anderson

Changes and Corrections

p. 73 Figure 4.5. Obviously, the labels on the tangent line should be $d\mathbf{U}_{\mathrm{S,V}} = 0$ and $d\mathbf{S}_{\mathrm{U,V}} = 0$, not $d\mathbf{U}_{\mathrm{S,V}} = 0$ and $d\mathbf{U}_{\mathrm{U,V}} = 0$. This is made clear in the text.

p. 85 A footnote on this page mentions that enthalpy is a thermodynamic potential which is minimized for processes at constant S and P, but that it is never used in this sense. "Rarely" would be better than "never". See Stolper and Asimow (2007)[1] for an interesting use of enthalpy as a thermodynamic potential.

p. 87 Here is a serious error. The text says "It (*the cycle in Figure 4.11*) represents the ideal, or maximum work that can be attained by any engine, one in which 100% of the heat applied is converted into work." This is incorrect. Heat can never be converted completely into work. The explanation from the answer to question 8 in the problem set for this Chapter (*ans_ch_4.pdf*), is:

The fact that $q = -w$ does not mean that you have 100% heat to work conversion in a Carnot cycle. The heat lost from the cycle under the lower isotherm (500°C in this case) is "lost", and is unavailable for doing work. Therefore the work accomplished by the Carnot heat engine (the area of the cycle) must always be less than the heat input (the area under the upper isotherm on a TS diagram), and the "efficiency", or the fraction of heat transformed into work, is governed entirely by how far apart the upper and lower isotherms are.

More details are available in the *ans_ch_4.pdf* file.

Box on p. 96 I think now that what it says in this box, while true, must be a bit mysterious to readers. It says that the maximum amount of non-*PV* work that the reaction between corundum and water to produce gibbsite can produce is 16,523 J mol^{-1}. But the question occurs, how could this reaction be made to produce any useful work at all? The statement is technically true, but it is a bad example. Only some reactions can actually be made to do non-*PV* work. A better example would be the burning of octane (C_8H_{18}) in oxygen. If this is done in a calorimeter it does no non-*PV* or useful work, but if done in an internal combustion engine, it does. This concept should be then related to equation (4.57), which says that $\Delta G_{T,P}$ gives the maximum work that can be achieved from any reaction, such as burning octane, and equation (4.58), which says that even if you don't arrange things so that this work is actually done $\Delta G_{T,P}$ will still be a negative quantity.

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[1] Insights Into Mantle Melting From Graphical Analysis Of One-Component Systems. American Journal of Science, v. 307, October, 2007, pp. 1051-1139; DOI 10.2475/08.2007.01

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, if $c = 2$ and $p = 2$, then $f = 2$, 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. 363 Figure 12.9. The $\log f_{O_2}$ numbers on the contours should all be negative.

p. 386 The h° and s° terms in the equation preceding (13.42) should be h°_0 and s°_0.

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.

p. 568–569 The units of the entries in Table 18.3, and the labels on the y-axis in Figures 18.8 and 18.9 are $\mathrm{J\,mol^{-1}}$, which might be confusing if you recall that **G** is defined as total system Gibbs energy and therefore has units of Joules, which depends on how much of the system there is, i.e., how many moles of each component. In this case the system has been defined as containing $(4-2\xi)$ moles of N_2, H_2 and NH_3, so **G** in $\mathrm{J\,mol^{-1}}$ in this case means Gibbs energy in Joules per $(4-2\xi)$ moles of this system. When $\xi = 0$ **G** is the Gibbs energy in Joules of a mixture of 1 mole of N_2 and 3 moles of H_2, and when $\xi = 1$, **G** is Joules per 2 moles of NH_3.

p. 632 Missing from References:
Helgeson, H.C., 1991, Organic/inorganic reactions in metamorphic processes. Canadian Mineralogist, v. 29, pp. 707–739.

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 $-\mathscr{A}\,d\xi$) might or might not be used to do work. This is expanded upon in §7 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. ΔH_3 should actually be $\Delta H_2 - \Delta H_1$ rather than $\Delta H_1 - \Delta H_2$, in order that ΔH_3 (for the reaction $\mathrm{A} + \mathrm{B} \rightarrow \mathrm{AB}$) be negative, that is, exothermic.

p. 142 Equation 5.33: A plus sign (+) is missing between $S^{\circ}_{T_\mathrm{r},i}(T - T_\mathrm{r})$ and a_i.

p. 145 In equation (5.41) the subscripts on the right side are interchanged. It should read

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

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

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

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, $(T1000)^2$ in the final term should be $(T/1000)^2$.

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 $83.1451\,\mathrm{cm^3\,bar\,K^{-1}\,mol^{-2}}$. The units of a are thus $\mathrm{cm^6\,bar\,mol^{-2}}$, and of b are $\mathrm{cm^3\,mol^{-1}}$. These parameters are often reported in units of $\mathrm{J\,m^3\,mol^{-2}}$ and $\mathrm{m^3\,mol^{-1}}$, respectively, where

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

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 fom 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 N_2 and 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 $A \to A'$, 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 ξ, the slope of the curve in Figure 18.8. What I meant to say was that it is the affinity *term*, $-\mathscr{A}\,d\xi$, 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 $140.87\,\mathrm{cm^3\,mol^{-1}}$, 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 Appemdix 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 $KAlSi_2(AlSi_3)O_{10}(OH)_2$, pyrophyllite $Al_2Si_4O_{10}(OH)_2$, and illite $K_2(Al_7Mg)(Si_{14}Al_2)O_{40}(OH)_8$ between 15 and 375 K, and their standard entropies at 298.15 K. U.S. Geological Survey Jour. Research v.4, pp. 631–644.