A Workbook for Chemical Reaction Equilibria

The motivation for this project derives from Paper 59c at the AIChE Meeting in Los Angeles, November, 2000, by V.A. Burrows and G.B. Raupp. The concept is to provide a self-contained tutorial supplement to the Elliott-Lira textbook similar in format to the kinds of workbooks that should be familiar from K-12 education. Basically, the material should be presented in whatever manner makes the students feel most comfortable. The important thing is that they learn the material.

The intent is to briefly supplement the discussion in the text, then provide example problems to illustrate in great detail how a particular analysis is performed. Exercise problems immediately following each example are designed to look very similar to the example, instantly reinforcing the principles covered in the example. The disadvantage of this approach is that it discourages the independent thought and analysis process that engineers must ultimately develop. Note, however, that this is a supplement to the existing text. The existing homework problems remain as general statements like homework problems in any text.

Clearly there is more work involved for students who pursue the workbook. There is nothing wrong with that if the workbook provides a path for students to learn the material who might not have learned it otherwise. Hence, we suggest that the workbook not be a required element for all students, but completion of the workbook might gain recognition in a small component of the overall grading such as “class participation.” Long term, it would be very interesting to study how student success correlates with completion of the workbook. We would expect a significant correlation that might depend on the interaction between overall grade in the course and completion of the workbook.

The specific chapter covered by this particular workbook is Chapter 17, Reacting Systems. More than any other chapter, we have heard suggestions that the coverage in this chapter is quite broad, with insufficient examples to thoroughly grasp the principles. Addressing this concern is quite fitting within the workbook context since providing examples is what the workbook is all about. Note that we have included complete solutions to the practice problems stated in the text in addition to the additional workbook examples. With these complete solutions, combined with the additional workbook examples, the total number of solved examples is roughly tripled. We hope that these additions will help to relieve the difficulty perceived by students with this subject matter.

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17 Reacting Systems

17.1 Reaction Coordinate

The key point of this section is for you to review mole balances and their implications. You should be familiar with the basic concepts from courses in mass and energy balances (MEBs) and introductory chemistry so we do not dwell too long on all of these basics. The following questions should flesh out a few subtleties if you missed them.

17.1.1 Example. Consider the reaction CO + H2O = CO2 + H2.

(a) Identify ν_1-ν_4.
(b) If the initial moles of H2O:CO were 2:1, how would that affect the values of ν_1-ν_4?
(c) If the reaction were rewritten as 2CO + 2H2O = 2CO2 + 2H2, how would that affect the values of ν_1-ν_4?
(d) Reconsider the reaction CO + H2O = CO2 + H2, assuming a stoichiometric feed this time. A "stoichiometric feed" means that the reactants are fed in the ratio of their ν coefficients. In this case, that means moles of H2O:CO of 1:1, or 2:2, etc. Compute the mole fractions of all components assuming the extent of reaction is, ξ, 0.25. Also compute the ratio of product mole fractions to reactant mole fractions.
(e) Reconsider the reaction CO + H2O = CO2 + H2, assuming a feed in which the moles of H2O and CO are 2 and 1. Compute the mole fractions of all components assuming the extent of reaction, ξ, is 0.25. Also compute the ratio of product mole fractions to reactant mole fractions. What are the total moles going out of the reactor and the moles coming in?
(f) The "limiting reactant" is the reactant that is depleted first, hence stopping the reaction. If the initial moles of H2O:CO were 2:1, which component would be the limiting reactant?

Solution:

(a) ν1 = ν2 = -1; ν3 = ν4 = 1
(b) The initial moles do not affect the stoichiometric coefficients. Only the mole fractions are affected.
(c) Everything would be multiplied by two. Note that the Δ*G* value would also be doubled with the implication that the *Ka* value would be squared, since it is exp(-Δ*G*). All the mole fractions of products/reactants would also be squared because of being raised to the power of the stoichiometric coefficient.
(d) Making a table to keep track of the stoichiometry:

CO	1	-ξ
H2O	1	-ξ
CO2		ξ
H2		ξ
Tot	2+	0

$$y_{CO}=y_{H2O} = (1-\xi)/2 = 0.75/2 = 0.375$$
$$y_{CO2}=y_{H2} = \xi/2 = 0.125$$
$$\text{Products/reactants} = y_{CO2}*y_{HO}/(y_{CO}*y_{H2O}) = 1/9= 0.111$$

(e) Making a table to keep track of the stoichiometry:

CO	1	-ξ
H2O	2	-ξ
CO2		ξ
H2		ξ
Tot	3+	0

$$y_{CO}*y_{H2O} = (1-\xi)*(2-\xi)/9 = 0.1458$$
$$y_{CO2}*y_{H2} = \xi^2/9 = 0.0139$$
$$\text{Products/reactants} = y_{CO2}*y_{H2}/(y_{CO}*y_{H2O}) = 0.0952$$

(f) CO

17.1.2 Exercise. Consider the reaction N2 + 3H2 = 2NH3.

(a) Identify ν1-ν3.
(b) If the initial moles of H2:N2 were 2:1, how would that affect the values of ν1-ν3?
(c) If the reaction were rewritten as ½ N2 + 3/2 H2 = NH3, how would that affect the values of ν1-ν3?
(d) Reconsider the reaction N2 + 3H2 = 2NH3, assuming a stoichiometric feed this time. A "stoichiometric feed" means that the reactants are fed in the ratio of their ν coefficients. In this case, that means moles of H2:N2 of 3:1. Compute the mole fractions of all components assuming the extent of reaction is, ξ, 0.25. Also compute the ratio of product mole fractions to reactant mole fractions.
(e) Reconsider the reaction N2 + 3H2 = 2NH3, assuming a feed in which the moles of H2 and N2 are 2 and 1. Compute the mole fractions of all components assuming the extent of reaction, ξ, is 0.25. Also compute

the ratio of product mole fractions to reactant mole fractions. What are the total moles going out of the reactor and the moles coming in?

(f) The "limiting reactant" is the reactant that is depleted first, hence stopping the reaction. If the initial moles of H2:N2 were 2:1, which component would be the limiting reactant?

17.1.3 Exercise. SO2 Oxidation

Air is a mixture of roughly 79%N2 and 21%O2 and a common feed component in oxidation reactions because it is inexpensive and readily available. One consideration is that the nitrogen in air is inert in most oxidation reactions. Suppose a feed of 30% SO2 and 70% air is fed to an oxidation reactor at 250°C and 0.15 MPa. You may wish to refer to Ex. 14.4 for an example that includes inerts.

(a) Write the balanced reaction for oxidation of SO2 to SO3.

(b) Write the stoichiometry table and express the mole fractions of all components in terms of the extent of reaction, ξ, (cf. Ex. 14.1).

(c) Which component is the limiting reactant?

(d) If the extent of reaction was 100%, what would be the composition and flow rate leaving the reactor?

17.2 Equilibrium Constraint

You should recall that the equilibrium constant is equal to products over reactants. For example, $K_w = [OH^-][H^+]/[H2O]$ should remind you of the decomposition of water into its ions, giving rise to the acidity and basicity that we commonly indicate by the pH. This section derives the equilibrium constant relationship from the general expression for Gibbs Energy of a mixture developed in Chapter 11. The basic idea is that the Gibbs energy is minimized at equilibrium. Taking the derivative of the Gibbs energy with respect to the extent of reaction gives the minimum Gibbs energy at the equilibrium extent.

Perhaps the most confusing point in the study of reacting systems is the way that the reference state gets buried. By assuming a reference state of the ideal gas at 1 bar, we save the trouble of computing the free energy and fugacity of the reference state. After all, the fugacity of any ideal gas at 1 bar is 1 bar. As a result, the ratio of product to reactant fugacities that comprises the equilibrium constant does not indicate anything about the reference state fugacity of 1 bar. After all, ratios divided by unity are just the same quantity as before the division. But now the reference state is invisible, it is buried in the tabulated values of $G_i°$ for each component. To stay out of trouble, you should perform all reaction equilibrium calculations in the same pressure units as the tabulated values of $G_i°$, at least until you completely comprehend reference states as discussed below. For this text, that means converting all pressure units to bars.

Besides converting to bars, one essential point is that the numerical value of K_a does not depend on the *process* pressure. Here is a little brain teaser. Suppose we write that $K_a = (y_{NH3}P)^2(y_{N2}P)^{-1}(y_{H2}P)^3$ for the ammonia synthesis reaction. Factoring out the pressure effect, we see that $K_a \sim P^{-2}$. So raising the value of pressure should decrease the value of K_a. Right? WRONG!!!!!!! This question fools about 50% of students, so don't feel too embarrassed if you missed it.[1] Eq. 17.20 shows that $K_a = \exp(-\Delta G_T°/RT)$. Now it is true that $\Delta G_T°$ does depend on the *reference state pressure*, but the reference state pressure is a single standard value regardless of what process you are running. How then can K_a possibly be independent of process pressure and still equal to the ratio of partial pressures of products over reactants? Answer: the mole fractions must change to compensate for the increase in pressure. For the ammonia synthesis reaction, this means the mole fraction of ammonia must increase. In other words, we can increase conversion by increasing pressure. This is why industrial processes for ammonia production operate at pressures above 100 bars. Ammonia is very important for fertilizer production, by the way.

Comprehending Reference States

Practically, you can solve a lot of problems without understanding all the subtleties of reference states. So you may want to put some of these detailed concerns on the back burner. Performing all calculations in bars circumvents the reference state problem temporarily, but you should not be afraid of understanding it properly. We learned that pressure affects the Gibbs energy of ideal gases as specified in Eq. 9.16. So, assuming a different value for the reference state pressure must give a different value for $G_i°$ in the obvious manner of Eq. 9.16. Suppose we wanted to use the ideal gas at 298.15K and 1 MPa as our reference state. Noting that 1 bar equals 0.1 MPa, the value of $G_i°$ would simply be $G_i°(1) = G_i°(0.1) + [G_i°(1)-G_i°(0.1)] = G_i°(0.1) + \ln(10)$. But wait. Applying that relation to, say, hydrogen would give a non-zero value for the element at its reference condition. It is conventional to set the reference state to zero for the elements at their reference conditions. So we need to subtract ln(10) from all compounds with H2 in them after adding ln(10). But wait. CH4, for example, has two H2's in it. So now what do we do? Would you believe… subtract 2ln(10)? So the value for G_f of CH4 would be: $-50.45 + \ln(10) - 2\ln(10) = -52.75$ kJ/mol in a table with standard state of 1MPa.

What about the C in CH4? Elemental carbon (C) is a solid. If you think back to why Gibbs energy depends on pressure, it is because Gibbs energy includes entropy. Entropy for an ideal gas depends on pressure because it changes as $-\ln(V_2/V_1)$. Remember the particles in boxes from Chapter 4? Think about a lump of coal; it is mostly elemental carbon. If you raised the pressure in a container with a lump of coal in it from 1 bar to 1 MPa, do you think the volume of the coal would change significantly? No way, it is as hard as a rock (because it is a rock). So zero volume change at constant temperature translates into no change in Gibbs energy for solids. The value of
–52.75kJ/mol for CH4 with a standard state of 1MPa stands. Pretty confusing? Yes, but you have really grasped the implications of reference states in general once you grasp this. These implications come up in Gibbs energy minimization (Ex. 17.12-13) and in the study of electrolytes (Chapter 18), so you might as well make yourself comfortable with the issue as soon as possible.

17.2.1 Example: K_a for CO + H2O = CO2 + H2.

(a) Look up the values of $G_f°$ at 298.15K for the above reaction make a table like the one in Ex 17.2
(b) Compute $\Delta G_{298}°$ and K_a for this reaction.
(c) Assuming $f_i = y_iP$, write the equation for K_a in terms of product to reactant mole fractions and pressure.

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[1] Don't be too embarrassed *this time*. Fooled you once, shame on me. Fool you twice, *shame on you*.

(d) Assuming a stoichiometric feed and expressing the mole fractions in terms of the reaction coordinate as in Ex 17.1, develop an equation relating the value of K_a to the extent of reaction.

Solution:

From Appendix E.1, most are in the "Gases" section:

	$\Delta H_{f,298}$ kJ/mol	$\Delta G_{f,298}$ kJ/mol
CO	-110.53	-137.16
CO2	-393.51	-394.38
H2	0	0
H2O	-241.835	-228.614

(b) $\Delta G_{298}°$ = -393.51 – (–110.53 -241.835 +0) = -28.606 kJ/mol

K_a = exp[+28.606*1000/(8.314*298.15)] = exp[-0.10578] = 102,744

(c) $K_a = (y_{CO2}\,P)\,(y_{H2}\,P)\,(y_{H2O}\,P)^{-1}\,(y_{CO}\,P)^{-1} = (y_{CO2}\,y_{H2})/(y_{H2O}\,y_{CO})$

(d) The stoichiometric feed means that 1 mole of CO is fed for every mole of H2O. To get mole fractions, we can assume a basis of 1 mole of feed for each. So $n_{CO} = 1-\xi$, $n_{H2O} = 1-\xi$, $n_{CO2} = \xi$, $n_{H2} = \xi$ and $n_T = 2$.

$K_a = \xi^2/(1-\xi)^2$.

17.2.2 Exercise. Consider the reaction N2 + 3H2 = 2NH3.

(a) Look up the values of $G_f°$ at 298.15K for the above reaction make a table like the one in Ex 17.2

(b) Compute $\Delta G_{298}°$ and K_a for this reaction.

(c) Assuming $f_i = y_i P$, write the equation for K_a in terms of product to reactant mole fractions and pressure.

(d) Assuming a stoichiometric feed and expressing the mole fractions in terms of the extent of reaction as in Ex 17.1, develop an equation relating the value of K_a to the extent of reaction.

17.2.3 Exercise. Air oxidation of SO2

Air is a common feed component in oxidation reactions because it is inexpensive and readily available. One consideration is that the nitrogen in air is inert in most oxidation reactions. Suppose a feed of 30% SO2 and 70% air is fed to an oxidation reactor at 250°C and 0.15 MPa and oxidized to SO3.

(a) Look up the values of $G_f°$ at 298.15K for the above reaction make a table like the one in Ex 17.2

(b) Compute $\Delta G_{298}°$ and K_a for this reaction.

(c) Assuming $f_i = y_i P$, write the equation for K_a in terms of product to reactant mole fractions and pressure.

(d) Assuming a stoichiometric feed and expressing the mole fractions in terms of the extent of reaction as in Ex 17.1, develop an equation relating the value of K_a to the extent of reaction.

17.2.4 Related Practice Problems

Check out the solutions to Practice Problems 17.1, 17.2, and 17.5.

17.3 Reaction equilibria for ideal solutions

The ideal solution assumption simply states that $\hat{f}_i = y_i P$ (Eq. 10.61) for gases or $\hat{f}_i = x_i P_i^{sat}$ for liquids when the Poynting correction is negligible (Eq. 10.73). The most commonly applied form for reactions is Eq. 10.61 because most reactions are carried out at high temperatures and low pressures. Substitution of Eq. 10.61 to generate a single equation in the single unknown ξ should be straightforward for you now. All that remains is to solve the equation. Perhaps you have done this for the previous examples already. If so, you can simply write your answers to the next couple of problems.

17.3.1 Example. Equilibrium conversion for the reaction CO + H2O = CO2 + H2.

(a) Solve the equation developed in the previous section for ξ of this reaction at 1 bar and 298.15K.
(b) Compute the equilibrium mole fractions of all components.

Solution:

(a) We left off with $K_a = \xi^2/(1-\xi)^2 = 102{,}744$. Cross-multiplying and rearranging gives a quadratic equation.
$(1/102{,}744-1)\xi^2 + 2\xi - 1 = 0 = -0.99999\xi^2 + 2\xi - 1 \Rightarrow \xi = [-2 \pm (4-4*0.99999*1)^{½}]/(2*(-0.99999))$
We can eliminate the negative root because it would give negative values for the mole fractions of products. Then, $\xi = [-1+(1.1116)^{½}]/0.1116 = 0.99689$. This reaction strongly favors products at these conditions.
(b) Recalling, $n_{CO} = 1-\xi$, $n_{H2O} = 1-\xi$, $n_{CO2} = \xi$, $n_{H2} = \xi$ and $n_T = 2$:
$y_{CO} = y_{H2O} = (1-\xi)/2 = 0.0016$, $y_{CO2} = y_{H2} = \xi/2 = 0.4984$

17.3.2 Exercise. Consider the reaction N2 + 3H2 = 2NH3.

(a) Assuming ideal solution estimates for the component fugacities, solve the equation developed in the previous section for ξ of this reaction at 1 bar and 298.15K and 5 MPa.
(b) Compute the equilibrium mole fractions of all components.

17.3.3 Exercise. Air oxidation of SO2

Air is a common feed component in oxidation reactions because it is inexpensive and readily available. One consideration is that the nitrogen in air is inert in most oxidation reactions. Suppose a feed of 30% SO2 and 70% air is oxidized to SO3 at 250°C and 0.15 MPa.

(a) Assuming ideal solution estimates for the component fugacities, solve the equation developed in the previous section for ξ of this reaction at 1 bar and 298.15K and 5 MPa.
(b) Compute the equilibrium mole fractions of all components.

17.3.4 Related Practice Problems

Check out the solutions to Practice Problems 17.1, 17.2, and 17.5.

17.4 Temperature Effects

One of the essential relations that you must assimilate thoroughly is the van't Hoff relation, especially the part about the extent of reaction increasing with temperature for endothermic reactions and decreasing for exothermic reactions. It is straightforward to apply Eqs. 3.46 and 17.28 when the heat capacities are expressed as third order polynomials, but could you develop your own expressions analogous to Eqs. 3.46 and 17.28 if you were given different expressions for the heat capacities?.

17.4.1 Example. Temperature dependence for the reaction CO + H2O = CO2 + H2.

(a) Compute the values of ΔG, ΔH, and K_a of this reaction at 1 bar and 400K.
(b) Compute the values of ΔG, ΔH, and K_a of this reaction at 1 bar and 500K.

Solution: This example is extremely similar to Example 17.4. Try to solve it yourself without looking at the solution below, then check your answers for errors.

	$\Delta H_{f,298}$ kJ/mol	$\Delta G_{f,298}$ kJ/mol	*a*	*b*	*c*	*d*
CO2	-393.51	-394.38	1.98E+01	7.34E-02	-5.60E-05	1.72E-08
H2	0	0	0	0	0	0
CO	-110.53	-137.16	3.09E+01	-1.29E-02	2.79E-05	-1.27E-08
H2O	-241.835	-228.614	32.24	1.92E-03	1.06E-05	-3.60E-09
Δ	-41.145	-28.606	-16.17	9.364E-02	-1.083E-04	4.111E-08

(a) From WB Ex. 17.2.1, we have $\Delta G_{298}°$ = -28.606 and K_a^{298} = 102,744. Referring to the values of ΔH in Appendix E.1, $\Delta H_{298}°$ = -393.51 + 0 – (-110.53 –241.835) = -41.145 kJ/mol. Similar operations yield the values for Δa-Δd in the table above. Substituting into Eq. 3.46,

-41.145*1000 = J*1000 – 16.17*298.15 +0.09364*298.15^2/2 – 1.083E-4*298.15^3/3 + 4.111E-8*298.15^4/4

$\Rightarrow J$ = -39.611 kJ/mol. Note that we multiply by 1000 to convert from kJ/mol to J/mol.

$\Delta H_T°$ (J/mol) = -39,611 + 16.17 T – 0.04682*T^2 + 0.3610E-4*T^3 – 1.0278E-8 *T^4

Substituting into Eq. 17.28,

-28.606*1000/(8.314*298.15) = -39.611*1000/(8.314*298.15) + 16.17*ln(298.15)/8.314 – 0.09364*298.15/(2*8.314) + 1.083E-4*298.15^2/(6*8.314) – 4.111E-8*298.15^3/(12*8.314) + I

$\Rightarrow I$ = -5.145

The resulting formula is,

$\Delta G_T°$ (J/mol) = -39,611 + 16.17 T ln$T$ – 0.04682*T^2 + 0.1805E-4*T^3 – 0.3426E-8 *T^4 - -42.776 T

Evaluating at 400 K, $\Delta G_{400}°$ = -24.392 kJ/mol, $\Delta H_{400}°$ = -40.634 kJ/mol, K_a = 1532

(b) The beauty of developing the general formula is that computing K_a at different temperatures becomes easy. Evaluating at 500 K, $\Delta G_{500}°$ = -20.416 kJ/mol, $\Delta H_{500}°$ = -39.859 kJ/mol, K_a = 136

17.4.2 Example. Consider the reaction N2 + 3H2 = 2NH3.

(a) Compute the values of $\Delta G°$, $\Delta H°$, and K_a of this reaction at 100 bar and 600K.
(b) Assuming ideal solution estimates for the component fugacities and a stoichiometric feed, solve for ξ of this reaction at 600K and 10 MPa.

Solution:
(a) The procedure from Ex. 17.4 can be repeated for hand calculations, but this quickly becomes tiresome. The spreadsheet Kcalc.xls minimizes the tedium. The table below summarizes the values from the spreadsheet.

	$\Delta H_{f,298}$ kJ/mol	$\Delta G_{f,298}$ kJ/mol	*a*	*b*	*c*	*d*
NH3	-45.94	-16.4013	27.31	0.02383	1.71E-05	-1.19E-08
H2	0	0	27.14	0.00927	-1.38E-05	7.65E-09
N2	0	0	31.15	-0.01357	2.68E-05	-1.17E-08
Δ	-91.880	-32.803	-57.95	0.03341	4.877E-05	-3.496E-08

Evaluating at 600 K, $\Delta G_{600}° = 31.685$ kJ/mol, $\Delta H_{600}° = -102.827$ kJ/mol, $K_a = 0.00174$. This value will be different from the values in Ex 17.9 for two reasons: (1) the reaction in Ex 17.9 is written as $\frac{1}{2} N_2 + {}^{3}/_{2} H_2 = NH_3$, so this 0.00174 should be the square of the value for the reaction in Ex 17.9; (2) the values in Ex 17.9 were computed by the shortcut equation discussed later. We have computed a more precise value.
Note that the *process* pressure of 100 bar has no impact on K_a, etc. This information is impertinent for this calculation. Did it confuse you? Shame on you if it did.
(b) Remember: Our reference state pressure is in bar, so we should convert from 10 MPa to 100 bars. Then,
$y_{N2} = (1-\xi)/(4-2\xi)$; $y_{H2} = (3-3\xi)/(4-2\xi)$; $y_{NH3} = 2\xi/(4-2\xi)$;
$K_a = (2\xi)^2(4-2\xi)^2/[(3-3\xi)^3(1-\xi)] = 16\xi^2*(2-\xi)^2/[27(1-\xi)^4] = 100^2*0.00174$. We can simplify if we multiply by 27/16 and take the square root of both sides. Then, $\xi(2-\xi) = 5.4187(1-\xi)^2$. Solving the quadratic gives: $\xi = 0.605$

17.4.3 Exercise. Air oxidation of SO2

Air is a common feed component in oxidation reactions because it is inexpensive and readily available. One consideration is that the nitrogen in air is inert in most oxidation reactions. Suppose a feed of 30% SO2 and 70% air is oxidized to SO3 at 250°C and 0.15 MPa.

(a) Compute the values of $\Delta G°$, $\Delta H°$, and K_a of this reaction at 250°C and 0.15 MPa.
(b) Assuming ideal solution estimates for the component fugacities, solve for ξ of this reaction at 250°C and 0.15 MPa.
(c) Compute the equilibrium mole fractions of all components.

17.4.4 Related Practice Problems

Check out the solution to Practice Problems 17.3 and 17.4.

17.5 Shortcut Estimation of Temperature Effects

It is quite typical for chemical processes to be operated for long periods of time at very similar conditions. With this stipulation, it is often convenient to have a simpler equation than the complete equation with all terms. The shortcut van't Hoff equation can be convenient in this way, but it is valuable to apply the shortcut equation accurately. Like any approximate equation, it is most accurate near the conditions at which it is developed. If we have sufficient data to compute the K_a value at a temperature near the process conditions, accuracy is improved by doing so. The result is a simple but reliable equation in the form of $K_a = A + B/T$.

17.5.1 Example. Temperature dependence for the reaction CO + H2O = CO2 + H2.

(a) Compute the values of A, B in $K_a = A + B/T$ of this reaction at 1 bar and 400K.
(b) Compute the values of A, B in $K_a = A + B/T$ of this reaction at 1 bar and 500K. Compare the values of A, B to those from part (a). Also estimate the K_a value at 400K from the shortcut equation centered at 500K and compare it to the value from part (a).

Solution:
(a) Recalling at 400 K, $\Delta G_{400}^\circ = -24.392$ kJ/mol, $\Delta H_{400}^\circ = -40.634$ kJ/mol, $K_a = 1532$
$\ln(K_a) = \ln(1532) + (+40{,}634/8.314)*(1/T - 1/400) = 4887/T - 12.219$; $A = -4.885$; $B = 4887$
(b) Recalling at 500 K, $\Delta G_{500}^\circ = -20.416$ kJ/mol, $\Delta H_{500}^\circ = -39.859$ kJ/mol, $K_a = 136$
$\ln(K_a) = \ln(136) + (+39{,}859/8.314)*(1/T - 1/500) = 4794/T - 9.588$; $A = -4.676$; $B = 4794$
The value of A decreases slightly with temperature and B increases. Because these contributions are opposite in sign, their changes may cancel in large part. Considering the value of K_a at 400K estimated by the A, B from part (b), we have $K_a^{400} \sim 1494$. This is different from the value of 1532 in the third significant figure.

17.5.2 Example. Consider the reaction N2 + 3H2 = 2NH3.

(a) Compute the values of A, B in $K_a = A + B/T$ of this reaction at 1 bar and 600K.
(b) Compute the values of A, B in $K_a = A + B/T$ of this reaction at 1 bar and 700K. Compare the values of A, B to those from part (a).
(c) Also estimate the K_a value at 600K from the shortcut equation centered at 298.15 K and compare it to the value from part (a). Comment on the result.

Solution:
(a) Recalling at 600 K, $\Delta G_{600}^\circ = 31.685$ kJ/mol, $\Delta H_{600}^\circ = -102.827$ kJ/mol, $K_a = 0.00174$.
$\ln(K_a) = \ln(0.00174) + (+102{,}827/8.314)*(1/T - 1/600) = 12368/T - 26.967$; $A = -26.965$; $B = 12368$
(b) At 700 K, $\Delta G_{700}^\circ = 54.310$ kJ/mol, $\Delta H_{700}^\circ = -105.351$ kJ/mol, $K_a = 8.855\text{E-}5$
$\ln(K_a) = \ln(8.855\text{E-}5\ ) + (+105{,}351/8.314)*(1/T - 1/700) = 12672/T - 27.434$; $A = -27.434$; $B = 12672$
The value of K_a at 600 K estimated from the shortcut equation centered at 700K is 0.00181. This is varying in the second significant figure from the value of 0.00174.
(c) At 298.15K, $\Delta G_{700}^\circ = -32.803$ kJ/mol, $\Delta H_{700}^\circ = -91.880$ kJ/mol, $K_a = 558{,}162$.
$\ln(K_a) = \ln(558{,}162) + (+91{,}880/8.314)*(1/T - 1/298.15) = 11051/T - 23.834$; $A = -23.834$; $B = 11051$. Using the shortcut approximation and extrapolating to 600K, $\ln(K_a) = -5.4149$; $K_a = 0.00445$. This value is in error by $(0.00445 - 0.00174)/(0.00174)\ (100\%) = 155\%$. The absolute magnitude is close, but the percentage error is large when the shortcut equation is used over large temperature ranges.

17.5.3 Exercise. Air oxidation of SO2

Air is a common feed component in oxidation reactions because it is inexpensive and readily available. One consideration is that the nitrogen in air is inert in most oxidation reactions. Suppose a feed of 30% SO2 and 70% air is oxidized to SO3 at 250°C and 0.15 MPa.

(a) Compute the values of ΔG°, ΔH°, and K_a of this reaction at 250°C and 0.15 MPa.
(b) Assuming ideal solution estimates for the component fugacities, solve for ξ of this reaction at 250°C and 0.15 MPa.
(c) Compute the equilibrium mole fractions of all components.

17.5.4 Related Practice Problems

Check out the solution to Practice Problems 17.3 and 17.4.

17.6 Energy Balances for Reactions

Most reactions of industrial interest are exothermic. This means that the heat of reaction must be balanced in some way. In an adiabatic reactor, the heat of warming the reactants balances the heat of reaction. Otherwise, some form of cooling removes the heat. Perhaps the catalyst is fluidized and sent through a regeneration reactor. Perhaps cooling tubes are placed in the reactor, but this tends to be expensive. Or perhaps the reaction is conducted in roughly adiabatic stages with heat removal between stages. It is actually somewhat rare that the reactor can be perfectly characterized as isothermal. Therefore, accurate models generally require simultaneous estimation of the energy evolution implicit in ΔH as well as the equilibrium limitations implicit in ΔG.

17.6.1 Example. Heat of reaction for CO + H2O = CO2 + H2.

The reaction of CO + H2O = CO2+ H2 is called the water-gas shift reaction. It is important in processes designed to enrich the hydrogen content of reformer effluents. Reforming is generally considered to be the conversion of natural gas or other hydrocarbons into some form of CO and H2. Reforming is relevant to the design of fuel cells as well as more traditional processes. We would like to estimate the number of tubes required to maintain a water-gas shift reactor at roughly 500K. The flowrate of the stoichiometric feed is to be 100 kmol/hr for both reactants combined. The heat transfer coefficient may be estimated as 250 W/m2-K and the temperature difference between the tubes and reactor is 100K. Tubes are available in 40 ft lengths and half-inch diameter. Assuming the entire reactor is to be held at the same temperature and concentration (well-mixed), how many tubes are required?

Solution:

Recalling at 500 K, $\Delta G_{500}°$ = -20.416 kJ/mol, $\Delta H_{500}°$ = -39.859 kJ/mol, K_a = 136

100 kmol/hr = 27.8 mol/s. The equilibrium conversion at 500K is given by $136(1-\xi)^2 = \xi^2 \Rightarrow \xi = 0.921$.

thus, the heat evolved is 0.921*39,859 J/mol*27.8mol/s = 1.020 MJ/s = 1.020 MW. Each tube has an area of 40ft*0.3048 m/ft *3.14*0.5 in*0.0254m/in = 0.486m^2 /tube. 250 W/m^2-K *100K * 0.486m^2/tube = 12155 W/tube

1,020,000 W/12155W/tube = 84 tubes. There's more engineering than thermo here, but that's okay.

17.6.2 Example. Heat generation in a catalytic converter

When designing a catalytic converter for automobile exhaust, it is important to consider the heat evolution and the temperature maintained in the catalytic converter. The key reaction is CO + ½ O2 = CO2. Suppose 600 ppm (mole basis) of CO in 75% N2 with remainder CO2 enter the reactor at 600K and are completely and adiabatically converted to CO2. What would be the temperature of the exhaust stream?

Solution:

Referring to Kcalc.xls at 600 K, $\Delta H_{600}°$ = -283.648 kJ/mol. The K_a value is very large, indicating complete conversion. We can estimate the C_P value as 0.75*30+0.25*47 = 34 J/mol-K Basis: 1 mole of feed to the converter.

0.000600 moles CO * 283,648 J/mol = 34 *(T-600) $\Rightarrow T$ = 605 K.

17.6.3 Exercise. Air oxidation of SO2

Air is a common feed component in oxidation reactions because it is inexpensive and readily available. One consideration is that the nitrogen in air is inert in most oxidation reactions. Suppose a feed of 30% SO2 and 70% air is oxidized to SO3 at 250°C and 0.15 MPa. The heat transfer coefficient may be estimated as 250 W/m2-K and the temperature difference between the tubes and reactor is 100K. Tubes are available in 40 ft lengths and half-inch diameter. Assuming the entire reactor is to be held at the same temperature and concentration (well-mixed), how many tubes are required?

17.7 General Observations about Pressure Effects

The ideal solution approximation suffices for most gas phase reactions, but may become inaccurate at high pressures if K_ϕ deviates significantly from unity. As noted in the text, this is unlikely since the deviations in the numerator tend to be canceled by the deviations in the denominator. To get some feel for the conditions when K_ϕ needs to be considered, we consider the following examples.

17.7.1 Example. K_ϕ for CO + H2O = CO2 + H2.

(a) Use the Peng-Robinson equation to estimate K_ϕ at 500K and 10 bars.
(b) Use the Peng-Robinson equation to estimate K_ϕ at 500K and 100 bars.

Solution:

(a) Using PRFUG.xls option assuming equimolar compositions, we get
$K_\phi = \phi_{CO2}\phi_{H2}/(\phi_{CO}\phi_{H2O}) = 0.9928*1.0068/(1.006*0.9744) = 1.0197$

Note that $\phi_i = \hat{f}_i/y_iP$, so we must divide the fugacities from the program appropriately.

(b) Using PRFUG.xls option assuming equimolar compositions, we get $K_\phi = \phi_{CO2}\phi_{H2}/(\phi_{CO}\phi_{H2O}) = 0.9390*1.06988/(1.0672*0.7771) = 1.3798$

Basically, the deviation from unity is dominated by the fugacity coefficient of water because it is the only component that is not above its critical temperature.

17.7.2 Example. K_ϕ for N2 + 3H2 = 2NH3

(a) Use the Peng-Robinson equation to estimate K_ϕ at 600K and 10 bars.
(b) Use the Peng-Robinson equation to estimate K_ϕ at 600K and 100 bars.

Solution:

(a) Using PRFUG.xls option assuming equimolar compositions, we get
$K_\phi = \phi_{NH3}^2/(\phi_{CO}\phi_{H2}^3) = 0.96812^2 /(1.0368*1.0277^3) = 0.8329$

Note that $\phi_i = f_i/y_iP$, so we must divide the fugacities from the program appropriately.

(b) Using PRFUG.xls option assuming equimolar compositions,we get $K_\phi = \phi_{NH3}^2/(\phi_{CO}\phi_{H2}^3) = 0.9842^2/(1.0773*1.0570^3) = 0.7016$

In this case, the numerator is subcritical, but the denominator is highly supercritical, so the asymmetry causes the deviation from unity.

17.7.3 Exercise. Air oxidation of SO2

(a) Compute K_ϕ for the SO2 oxidation reaction at 250°C and 0.15 MPa.
(b) Compute K_ϕ for the SO2 oxidation reaction at 250°C and 15 MPa.

17.7.4 Related Practice Problems

Check out the solution to Practice Problems 17.6 and 17.7.

17.8 Multireaction Equilibria

Multiple reactions frequently occur in engineering design situations, but many courses in introductory thermodynamics skip this issue. That is really unfortunate, because isomerizations, control of waste stream effluents, and many other problems generally focus on trade-offs between various multireaction outcomes. The extension is fairly straightforward when solving the reactions explicitly as in Examples 17.6 and 17.7, but the Gibbs energy minimization method of Examples 17.12 through 17.14 represents a quite different approach to the whole problem and it is worth knowing about. The Gibbs minimization method is frequently applied in preliminary designs and you should know its advantages and limitations. It tends to be much more sensitive to initial guesses and precision of the formation energies than the explicit approach. But it is very desirable to simply list a number of possible products without deriving specific equations and reaction energies during preliminary stages, especially if the preliminary calculation indicates that several of the possible products are not likely to form. Then you can avoid deriving specifics for those products if you do decide to apply the explicit method during later stages. The examples below explore the explicit method in a couple of instances and the Gibbs minimization method in a few more instances.

17.8.1 Example. Formaldehyde Decomposition

Formaldehyde and water are fed in a 2:1 molar ratio at 355°C and 1 bar, reacting to form methanol, formic acid, and methy formate. The reactions may be written as:

2HCHO + H2O = CH3OH + HCOOH

2HCHO = HCOOCH3

(a) For the reactions at 355°C and 1 bar, derive numerical values for *A* and *B* in the expression: $\ln Ka_i = A+B/T$, where T [=] K.(5)

(b) Write expressions for the extents of both reactions in terms of the values for Ka_1 and Ka_2. (5)

(c) Solve for the extents of reaction and the mole fractions of all species exiting the reactor. (10)

Compo	H_f(298)kJ/mol	G_f (298)kJ/mol	C_P^A(J/mole-K)	C_P^B	C_P^C	C_P^D
Formaldehyde	-116.0	-110.0	23.48	0.0316	2.985E-5	-2.300E-8
Methyl Formate	-352	-295	1.632	0.2700	-1.949E-4	5.702E-8
Formic Acid	-378.9	-351.2	11.71	0.1358	-8.411E-5	2.017E-8

Solution:

Substituting these values into the Kcalc.xls workbook and setting the temperature to T = (273.15+355) = 628.15,

(a) $\ln Ka_1 = -17.141+12943/T$; $\ln Ka_2 = -16.16 + 13992/T$.

(b)
$$Ka_1 = 17.29 = \frac{(3-\xi_1-\xi_2)^3}{(1-\xi_1)2^2(1-\xi_1-\xi_2)^2}\frac{\xi_1^{\,2}}{(3-\xi_1-\xi_2)^2} = \frac{\xi_1^{\,2}(3-\xi_1-\xi_2)}{4(1-\xi_1)(1-\xi_1-\xi_2)^2}$$

$$Ka_2 = 132.8 = \frac{(3-\xi_1-\xi_2)^2}{2^2(1-\xi_1-\xi_2)^2}\frac{\xi_2}{(3-\xi_1-\xi_2)} = \frac{\xi_2(3-\xi_1-\xi_2)}{4(1-\xi_1-\xi_2)^2}$$

(c) Typing these constraints into DualRxn spreadsheet and calling solver, $\xi_1 = 0.20$, $\xi_2 = 0.76$.

17.8.2 Exercise. Amine Synthesis By Explicit Reactions

Ammonia (NH3) and methanol (CH3OH) are fed in a 3:1 molar ratio at 355°C and 1 bar, reacting over a moderately selective catalyst to form water, methylamine (CH3NH2), and dimethylamine [$(CH3)_2$-NH]. The reaction may be written as:

NH3+ CH3OH= H2O + CH3NH2

CH3NH2+ CH3OH= H2O + $(CH3)_2$NH

(a) For these reactions at 355°C and 1 bar, derive numerical values for A and B in the expression: $\ln Ka = A+B/T$, where T [=] K.(5)

(b) Write expressions for the extents of both reactions in terms of the values for Ka_1 and Ka_2. (8)

(c) Solve for the extents of reaction and the mole fractions of all species exiting the reactor. (7)

Compo	H_f(298)J/mol	G_f (298)J/mol	Cp(J/mole-K)
methanol	-200,940	-162,320	55.5
ammonia	-45,898	-16,401	40.2
methylamine	-22,970	32,070	68.9
dimethylamine	-18,450	68,390	96.7
water	-241,820	-228,590	34.7

17.8.3 Example. Isomers Of Xylene And Ethylbenzene

Based on a feed of 111 kmol/hr of pure ethylbenzene, all xylene isomers and ethylbenzene exit the reactor in their equilibrium proportions. Estimate the mole fractions of each component exiting the reactor at 355°C and 1 bar. The reactor operates isothermally at 355°C and 1 bar. The equilibrium distribution of all species is to be studied by Gibbs energy minimization.

a. Write the atom balance constraints for all elements.(5)
b. Compute the relevant G_{fi}/RT.(8)
c. Solve for the mole fractions of all species exiting the reactor.(7)

Compo	C_P^A(J/mole-K)	C_P^B	C_P^C	C_P^D	H_f(298)kJ/mol	G_f (298)kJ/mol
o-xylene	-15.85	0.5962	-3.443E-4	7.528E-8	19.00	122.2
m-xylene	-29.17	0.6297	-3.747E-4	8.478E-8	17.25	118.9
p-xylene	-25.09	0.6042	-3.374E-4	6.820E-8	17.96	121.2
Ethylbenzene	-43.10	0.7072	-4.811E-4	1.301E-7	29.81	130.7

Solution:
a. H-bal: 10*sum(n_i) = 10; C-bal: 8*sum(n_i)=8.
b. Typing the values into Kcalc.xls and noting in each case the formation reaction is 8C + 5H2 = C8H10, where C8H10 refers to different isomers for different reactions:

Compo	G_f (628.15)kJ/mol
o-xylene	47.150
m-xylene	46.339
p-xylene	46.506
Ethylbenzene	48.316

c. Calling the solver we have

Compo	y_i
o-xylene	0.179
m-xylene	0.416
p-xylene	0.346
Ethylbenzene	0.059

17.8.4 Exercise. Amine Synthesis by Gibbs Minimization

Based on a feed of 1:3 kmol/hr of methanol:ammonia, methylamine [CH3NH2], dimethyl amine [$(CH3)_2$-NH], and trimethyl amine[$(CH3)_3$-N] exit the reactor along with unreacted feed components, all in their equilibrium proportions. Estimate the mole fractions of each component exiting the reactor at 355°C and 1 bar. The reactor operates isothermally at 355°C and 1 bar. The equilibrium distribution of all species is to be studied by Gibbs energy minimization.

a. Write the atom balance constraints for all elements. (5)
b. Assuming constant heat capacities as given below, estimate the relevant G_{fi}/RT.(8)
c. Taking an initial guess of zero conversion, solve for the mole fractions of all species exiting the reactor.(7)

Compo	H_f(298)J/mol	G_f (298)J/mol	Cp(J/mole-K)
methanol	-200,940	-162,320	55.5
ammonia	-45,898	-16,401	40.2
methylamine	-22,970	32,070	68.9
dimethylamine	-18,450	68,390	96.7
trimethylamine	-23,849	98,910	128.3
water	-241,820	-228,590	34.7

17.8.5 Related Practice Problems

Check out the solution to Practice Problems 17.6 and 17.7.

17.9 Sample Tests

17.9.1 Test 1 (1 hr)

1. Water (H2O) and 2-butanol (CH3CH2CH2CH2OH) are fed in a 1:10 molar ratio at 171°C and 11 bar, reacting over a catalyst to form water and 1-butene (CH3CH2CH=CH2). Note that for 2-butanol:

	$\Delta H^o_{f,298}$	$\Delta G^o_{f,298}$	Constants for C_P in J/mol-K			
Name	(kJ/mol)	(kJ/mol)	a	b	c	d
2-Butanol	-292.629	-167.611	5.748816	0.4242576	-0.0002327	4.77E-08

(a) Assuming only vapor species for this reaction at 171°C and 11 bar, derive numerical values for A and B in the expression: $\ln Ka = A+B/T$, where T [=] K.(5)
(b) Would raising the temperature favor products or reactants? (3)
(c) Would raising the pressure favor products or reactants? (3)
(d) Write an expression for computing the extent of reaction given Ka. (5)
(e) Solve for the extent of reaction and the mole fractions of all species exiting the reactor at 11 bar. (4)

2. Ethanol (CH3CH2OH), water (H2O) and 2-butanol (CH3CH2CH2CH2OH) are fed in a 100:1:10 molar ratio at 171°C and 11 bar, reacting over a catalyst to form ethylene (CH2=CH2), water, and 1-butene (CH3CH2CH=CH2). For the ethanol reaction at 171°C and 11 bar, numerical values are 15.78 and -5639 for A and B in the expression: $\ln Ka = A+B/T$, where T [=] K.
(a) Write expressions for the extents of both reactions in terms of the values for Ka_1 and Ka_2. (10)
(b) Solve for the extents of reaction and the mole fractions of all species exiting the reactor. (10)

3. Water (H2O) and 2-butanol (CH3CH2CH2CH2OH) are fed in a 1:10 molar ratio at 171°C and 11 bar, reacting over a catalyst to form 1-butanol, water and 1-butene (CH3CH2CH=CH2). The reactor operates isothermally at 171°C and 11 bar. The equilibrium distribution of all species is to be studied by Gibbs energy minimization.
a. Write the atom balance constraints for all elements. (5)
b. Estimate the relevant G_{fi}/RT for 1-butanol, the others are given below.(8)
c. Taking an initial guess of 70% conversion of 2-butanol and 0.0001 mole fraction of 1-butanol, solve for the mole fractions of all species exiting the reactor. Note: do not use ChemCad for this. (7)

Compo	G_f/RT
1-butanol	
1-butene	28.92173
2-butanol	-28.20177
water	-60.09647

17.9.2 Test 2 (1 hr)

1.a. Ethanol and acetic acid react to form ethyl acetate and water. Evaluate the Ka at 150°C.(5)

1.b. If the temperature of the above reaction was increased, would the extent of reaction tend to increase or decrease? Why? (5)

1.c. If the above reaction was carried out at atmospheric pressure and 150°C with a stoichiometric feed, what would be the equilibrium extent of reaction? (5)

2. It has been suggested that the number of C2 hydrocarbons formed during methane pyrolysis would be insufficient to explain the observed rate of carbon deposition even if they approached their maximum equilibrium limits. To evaluate the legitimacy of this suggestion, it is necessary to determine the maximum equilibrium compositions of these species.

(a) Perform this determination at 1 atm and 1500K considering the following species to be in mutual equilibrium: CH4, C2H6, C2H4, C2H2 and H2.(15)

(b) Would decreasing the pressure to 40 mmHg tend to enhance the equilibrium composition of C2 species, or diminish them? Why?(5)

3. Returning to the problem of ethyl acetate synthesis from acetic acid and ethanol at 150°C, what pressure must be maintained to keep 50% of the solution as a liquid and what will be the equilibrium compositions of the phases at these compositions? You may assume ideal solution behavior for the liquid phase with the short-cut vapor pressure approximation.(20)

(For ethyl acetate: T_c=523.2K, P_c = 37.8 bars and ω = 0.363)