

Gibbs Free Energy and Equilibrium in Chemical Systems¹

Minimalist Coverage *Basic Chemical Thermodynamics*, E. B. Smith,
Sections 4.1 – 4.4, 4.9 – 4.15

Longer Coverage *Physical Chemistry*, R. A. Alberty, 3rd ed, Sections 4.1–
4.6, 4.8, 5.1.

Homework: $1 \text{ atm} = 10^5 \text{ Nm}^{-2} = 760 \text{ mm Hg}$

1. Is the Gibbs Free Energy a State Function?
2. **Alberty, 4.9.** In Section 3.4 we calculated that the enthalpy of freezing water at -10C is -5619 Jmol^{-1} , and we calculated that the entropy of freezing water is $-20.54 \text{ JK}^{-1} \text{ mol}^{-1}$ at -10C . What is the Gibbs energy of freezing water at -10C ?
3. **Alberty, 4.10a, theory problem.** Integrate the Gibbs-Helmholtz equation to obtain an expression for ΔG_2 at temperature T_2 in terms of ΔG_1 at T_1 , assuming that ΔH is independent of temperature.
4. **Alberty, 4.11** When a liquid is compressed its Gibbs energy is increased. To a first approximation the increase in Gibbs energy can be calculated using $\left(\frac{\partial G}{\partial P}\right)_T = V$, assuming constant volume. What is the change in Gibbs energy for one mole of liquid water when it is compressed to 1000 atm (the density of water is approximately 1 g cm^{-3})?
5. **Alberty, 4.13** The standard entropy of $\text{O}_2(\text{g})$ at 298K and 1 atm is listed in Appendix C.2 as $205.138 \text{ JK}^{-1} \text{ mol}^{-1}$, and the standard Gibbs energy of formation is listed as 0 kJmol^{-1} . Assuming that O_2 is an ideal gas, what will be the entropy and Gibbs energy of formation for one mole of gas at 100 atm and 298K ?

¹Paul Maslen, Rm 428 B&S, ext 6282, maslen@crab.rutgers.edu
<http://crab.rutgers.edu/maslen/Courses/PChemI>

6. **Alberty, 4.14** One mole of helium is compressed isothermally and reversibly at $100C$ from a pressure of 2 to $10atm$. Calculate (a) Δq , (b) Δw , (c) ΔG , (d) ΔA , (e) ΔH , (f) ΔU and (g) ΔS , assuming that helium is an ideal gas.
7. **Alberty, 4.15** One mole of toluene is vaporized at its boiling point, $111C$. The heat of vaporization at this temperature is $361.9Jg^{-1}$. For the vaporization of one mole of toluene calculate (a) Δw , (b) Δq , (c) ΔH , (d) ΔU , (e) ΔG , (f) ΔS .
8. **Alberty, 4.16, theory question** If the Gibbs energy varies with temperature according to

$$G/T = a + b/T + c/T^2$$

how will the enthalpy and entropy vary with temperature? Check that these three equations are consistent.

(hint: review the derivation of the Gibbs-Helmholtz equation for the variation of G with temperature.)

9. **Alberty, 4.17** Calculate the change in Gibbs energy when one mole of supercooled water at $-3C$ freezes at constant T and P . The density of ice is $917 kg m^{-3}$, and its vapor pressure is $475Pa$. The density of supercooled water at $-3C$ is $999.6 kg m^{-3}$, and its vapor pressure is $489Pa$.

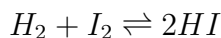
hint:

- (a) Calculate the volume of the solid and the liquid
- (b) Calculate ΔG along the following *reversible* path between the initial and final states:
 - i. Initial state is one mole of liquid at 1 atm.
 - ii. Next state is one mole of liquid at $489Pa$. $\Delta G = \int V_{\text{liquid}} dP$
 - iii. Next state is one mole of gas at $489Pa$. This is at equilibrium with the liquid, so what is ΔG ?
 - iv. Next state is one mole of gas at $475Pa$. $\Delta G = RT \ln(P_{\text{final}}/P_{\text{initial}})$.
 - v. Next state is one mole of solid at $475Pa$. This is at equilibrium with the gas, so what is ΔG ?
 - vi. Next state is one mole of solid at 1 atm. $\Delta G = \int V_{\text{solid}} dP$

10. **Alberty, 4.18** Calculate the Gibbs energy of fusion when one mole of supercooled water at $-3C$ freezes at constant T and P . The enthalpy of fusion of ice is $6000 J mol^{-1}$ at $0C$. The heat capacities of water and ice in the vicinity of the freezing point are 75.3 and $38 J K^{-1} mol^{-1}$ respectively.
11. **Alberty, 4.24** Calculate $\Delta_{\text{mix}}G$ and $\Delta_{\text{mix}}S$ for the formation of a quantity of air containing 1 mol of gas by mixing nitrogen and oxygen at $298K$. Air may be taken to be 80% nitrogen and 20% oxygen.
12. **Alberty, 4.25** A mole of gas A is mixed with a mole of gas B at 1 atm pressure and $298K$. How much work is required to separate these gases to produce a container of each at 1 atm and $298K$?
13. **Alberty, 4.29** Show that

$$\left(\frac{\partial U}{\partial S}\right)_V = \left(\frac{\partial H}{\partial S}\right)_P \quad \left(\frac{\partial H}{\partial P}\right)_S = \left(\frac{\partial G}{\partial P}\right)_T$$

14. **Alberty, 4.32** What is the effect of pressure on the entropy, enthalpy, and internal energy of an incompressible fluid?
15. **Alberty, 4.39** The heat of vaporization of liquid oxygen at its boiling point ($-183C$) at 1 atm is $6820 J mol^{-1}$. For the reversible vaporization of one mole of liquid oxygen calculate (a) Δq (b) ΔU (c) ΔS (d) ΔG .
16. The equilibrium constant for the reaction

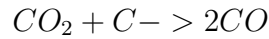


is 45.6 at $764K$ and is 60.8 at $667K$. Estimate the enthalpy change which accompanys one mole of the forward reaction.

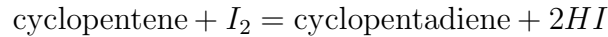
17. Formic acid is partially associated into dimers in the gas vapour phase. The mole fraction present as monomer is 0.228 at $283K$ and $10mm Hg$ pressure, and 0.715 at $333K$ and $16mm Hg$. Calculate the enthalpy change on dimerization.
18. In a mixture at 1 atmosphere the partial pressure of CO in equilibrium with CO_2 and C was as follows:

T/K	1083	1173	1253
Partial Pressure of CO/atm	0.931	0.978	0.991

Calculate the enthalpy change accompanying the reaction



19. For the gas phase reaction



$$\log K_p = 7.55 - 4817T^{-1}$$

in the temperature range $450 - 690K$.

Calculate the standard enthalpy, entropy and Gibbs Free Energy changes accompanying the reaction at $573K$.

20. **theory problem:** Show that for an ideal gas $\left(\frac{\partial U}{\partial V}\right)_T = 0$.

There are many ways to do this. One possible route is outlined here. Alternatively, figure out your own way, or follow Alberty. Show your working.

(a) Rearrange the combined first and second law:

$$dU = TdS - PdV$$

to express dS as a function of U and V .

(b) Take the $U \leftrightarrow T$ transform of dS to obtain a new state function, dX .

(c) Equate the two mixed second derivatives of X to obtain a Maxwell's relation, and rearrange to express $\left(\frac{\partial U}{\partial V}\right)_T$ in terms of P , T , and their derivatives.

(d) Show that $\left(\frac{\partial U}{\partial V}\right)_T = 0$ by making use of $PV = nRT$.

21. **theory problem:** Deduce a relation between C_V and C_P , valid for all materials (solids, liquids and gases).

- (a) Using $\delta q = TdS$, show that $C_V = T \left(\frac{\partial S}{\partial T} \right)_V$ and $C_P = T \left(\frac{\partial S}{\partial T} \right)_P$.
- (b) Starting from the ‘taylor series’:

$$dS(T, V) = \left(\frac{\partial S}{\partial T} \right)_V dT + \left(\frac{\partial S}{\partial V} \right)_T dV$$

divide through by dT at constant P , and hence express $\left(\frac{\partial S}{\partial T} \right)_P$ in terms of $\left(\frac{\partial S}{\partial T} \right)_V$, $\left(\frac{\partial S}{\partial V} \right)_T$ and $\left(\frac{\partial V}{\partial T} \right)_P$,

- (c) Obtain a Maxwell relation for $\left(\frac{\partial S}{\partial V} \right)_T$, by equating the mixed second derivatives of A , where

$$dA = -SdT + PdV$$

Substitute this expression for $\left(\frac{\partial S}{\partial V} \right)_T$ back into the expression for $\left(\frac{\partial S}{\partial T} \right)_P$.

- (d) Finally, substitute this expression for $\left(\frac{\partial S}{\partial T} \right)_P$ into the expression for C_P , and hence obtain a relation between C_P and C_V .
- (e) For an ideal gas, simplify the relation between C_P and C_V by using $PV = nRT$.