
Use of *Thermodynamics and Its Applications*, 3rd ed. and 10.40 class notes and handouts and a hand calculator are permitted. No other aids or documents are permitted. Please answer each question in a ~~separate~~ exam book. Be careful about managing your time and be aware of the maximum points allotted to each part of the 5 problems.

1. (20 points) Rocky and Rochelle Jones are having one of their heated arguments on thermodynamics. This time they are trying to reconcile the theoretical and empirical underpinnings of the so-called K factor charts or nomographs that were used during the last century, before computers were readily available, to characterize equilibrium phase partitioning in multicomponent distillation of hydrocarbons. K is defined as the equilibrium ratio of a particular component y_i in the vapor phase to x_i in the liquid phase. A typical nomograph is shown below for a set of light alkane and alkene hydrocarbons -- C-1 (methane) through C-9 (nonane),

Rocky claims that the K factors do a reasonable job of capturing important non-idealities over a wide range of conditions. In fact, Rocky notes that you only need the temperature and pressure to specify the vapor liquid equilibrium state as indicated by the nomograph. By connecting a straight line to a specific T and P , the intersection of that line with curve for each compound yields the $K = y_i/x_i$.

Rochelle adamantly maintains that the K 's are only based on single component information and that they fail to include intermolecular interactions.

We need your help to settle this argument.

(a) (10 points) Derive a general relationship for K in an n -component system vapor-liquid mixture at equilibrium. Clearly indicate the functional dependence of all derived parameters on measurable properties and state what type of constitutive property relationships are needed to evaluate K for each component.

(b) (10 points) For the P and T conditions given in the nomograph, who do you think is correct, Rocky or Rochelle? Explain.

(Image removed due to copyright considerations.)

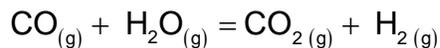
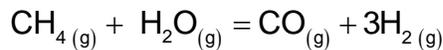
K-values for systems of light hydrocarbons

2. (20 points) MITY Industries is trying to decide where to make its next investments and has been approached by Colossal Technology Inc. (CTI), which claims that it has a new approach for generating motive power from hydrogen that is inherently more efficient than the traditional internal combustion (IC) engines that are in use today in our automobiles and trucks. In their scheme, pressurized pure hydrogen at 500 bar, 25°C is electrochemically oxidized with pure oxygen at 1 bar, 25°C to form water in a Fuel Cell Super Electro Converter (FCSEC) that generates electrical power directly. CTI claims that their concept can produce more power than even the most efficient IC engine using the same H₂ and O₂ feeds because the FCSEC converter is not subject to Carnot limitations. According to CTI, water exits the FCSEC at 1 bar, 25°C,

(a) (12 points) What do you think of CTI's claim? Back up your answer with appropriate thermodynamic analysis and discussion.

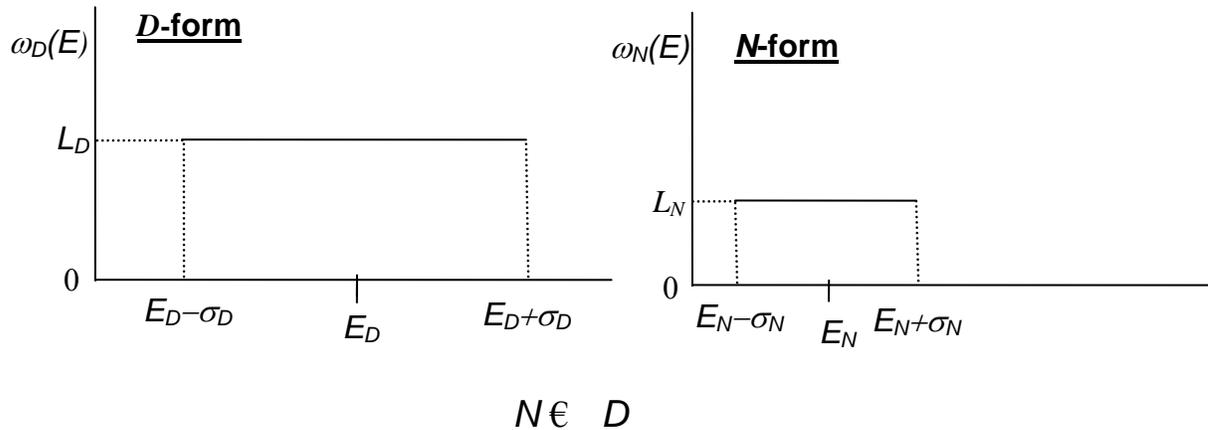
(b) (8 points) Pressurized methane, available at 500 bar and 25°C, has also been considered as a transportation fuel. CTI claims that they can chemically reform the methane to hydrogen via steam reforming on the vehicle and then use the FCSEC to produce electricity. Would using methane as a fuel introduce any additional thermodynamic limitations over using pure hydrogen? Explain your answer.

Steam reforming of methane proceeds by two dominant reaction pathways:



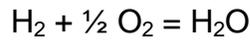
Feel free to use the thermochemical and other physical property available in Appendix G and elsewhere in the text.

3. (20 points) A protein system exists such that each protein molecule is either in its native form (N) or its denatured form (D). The N and D forms have different energy distributions (density of states) with the following structures:



(a) (10 points) Explain under what circumstances you would expect the chemical equilibrium constant to follow the van't Hoff equation ($\ln K$ vs. $1/T$ is a straight line). Back up your explanation with appropriate numerical analysis.

(b) (10 points) Describe briefly using appropriate equations how the situation would differ for the gas phase equilibrium that we discussed in class:

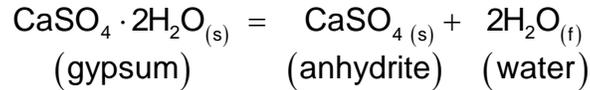


Recall: the semi-classical canonical partition function Q_N is given by

$$Q_N = \int_{-\infty}^{\infty} e^{-E/kT} \omega(E) d(E)$$

where $\omega(E)$ is the density of energy states.

4. (20 points) Important reactions between natural minerals occur under high pressure conditions in deep underground reservoirs in the presence of water. For many geologic systems the time scales are so long (typically years to centuries) that equilibrium can be safely assumed. One such system is the gypsum-anhydrite-water equilibrium where



In deriving the criteria for phase equilibrium, we found that the temperature and pressure of all phases were equal. In deeply located mineral systems in rock reservoirs, fluid phase pressures can be different than solid phase pressures if the rock column above the minerals is permeable to fluid. In other words, the hydraulic gradient and lithostatic gradient of pressure can be different. In this case, the system has one more degree of freedom and the equilibrium distribution of products and reactants at any particular depth depends on fluid pressure (P_f) and solid phase pressure (P_s) where both can be expressed as a function of depth z .

$$P_f = \int_0^z \rho_f g dz \quad \text{(hydraulic)}$$

$$P_s = \int_0^z \rho_s g dz \quad \text{(lithostatic)}$$

For the gypsum-anhydrite system, let's consider what happens over a range of conditions. The standard Gibbs free energy change for the reaction is given by Eq. (8-165):

$$\Delta G_{rx}^o(298 \text{ K}, 1 \text{ bar}) = \sum_{i=1}^n \nu_i \Delta G_{f,i}^o$$

Compound	$\Delta G_{f,i}^o$ (kJ/mol)
water H ₂ O (liquid)	-237.141
gypsum CaSO ₄ ·2H ₂ O (solid)	-1797.20
anhydrite CaSO ₄ (solid)	-1321.70

Reference states for all components are taken to be unit fugacity at 298 K, 1 bar pressure. The molar volume change for the solid phase gypsum to anhydrite transformation is:

$$\Delta V_{\text{gypsum} \rightarrow \text{anhydrite}} = V_{(\text{CaSO}_4)} - V_{(\text{CaSO}_4 \cdot 2\text{H}_2\text{O})} = -29.48 \text{ cm}^3/\text{mol}$$

and

$$V_{\text{H}_2\text{O, liquid}} = 18.07 \text{ cm}^3/\text{mol}$$

Over accessible depths, pressures ranged from 1 bar to as high as 1000 bar while temperatures can range from near ambient to 200°C.

(a) (10 points) Assuming that the standard state is now redefined at the temperature and pressure of the system, how will ΔG_{rx}° be affected by pressure at 298 K? Express your answer in terms of $\Delta G_{rx}^{\circ} = f(P_f, P_s)$.

(b) (10 points) For the cases of $\rho_s/\rho_f = 3.0$ and $\rho_s = \rho_f$; describe how you could estimate the variation of P_f with T for the gypsum to anhydrite transformation. What other property information is required to make the estimate? In both cases ρ_f can be taken as 1000 kg/m³.

[Hint: consider using the reaction equilibrium constraint $\sum v_i \mu_i = 0$ directly to determine a relationship between P_f and T assuming that all phases remain pure.]

5. (20 points) As described in class, we saw that the osmotic virial expansion of McMillan and Mayer provides a way to determine the osmotic pressure (Π) of a binary aqueous solutions for a range of solutes. Here we find

$$\frac{\Pi}{kT} = \rho_2 + B_2\rho_2^2 + B_3\rho_2^3 + \dots \quad (11-48)$$

$$\rho_2 \equiv \frac{N_A C_2}{M_2}$$

where N_A = Avogadro's number, C_2 = solute concentration in g/L, M_2 = molecular weight of the solute, B_2 = second osmotic virial coefficient, B_3 = third osmotic virial coefficient, etc. We can express the activity of the water solvent as $\ln a_w$ at some temperature, T, a reference pressure of 1 atm, and some concentration of the solvent:

$$\ln a_w = -\frac{\bar{V}_w \Pi}{RT}$$

where \bar{V}_w = molar volume of solvent (water).

Cryobiology researchers (J. Elliott, et al, 2003) have recently discovered that the osmotic virial equation can also be used to accurately estimate freezing point depression for a range of aqueous based biological systems. For example, freezing point depressions are correctly determined for macromolecular species such as hemoglobin and bovine serum albumin. The figure below shows experimental freezing point depression data for hemoglobin in water.

(a) (10 points) Develop an expression for the freezing point depression using the osmotic virial expansion. (Hint – both freezing point depression and osmotic pressure are colligative effects where the presence of solute lowers the chemical potential of the solvent in a similar manner)

(b) (10 points) By making appropriate assumptions regarding solute-solute interactions, use the freezing point depression data provided to estimate the excluded volume of a hemoglobin molecule. Be sure to clearly state the assumptions that you make.

Data:

$$V_w^L = 1.000 \times 10^{-3} \text{ L/g}$$

$$V_w^{ice} = 1.091 \times 10^{-3} \text{ L/g}$$

$$\Delta H_{fus,w} = 335 \text{ J/g}$$

$$M_{Hemoglobin} = 64,000 \text{ g/mol}$$

$$T_0 = \text{freezing point of pure water at 1 atm} = 273.15 \text{ K}$$

