

CYL100 2013–14 I semester Homework 3

Handed out: August 17, 2013

Due in: August 23, 2013

Notes: 1. Unless otherwise stated, gases can be considered to behave ideally.

2. You will need a table of thermodynamic data for some of the problems. Indicate the source of your thermodynamic data.

- Calculate the change in the chemical potential for N_2 , when the temperature changes from 298.15 K to 130 K and pressure changes from 1 atm to 600 atm. Treat nitrogen as a van der Waals gas with $a = 1.39000 \text{ L}^2 \text{ atm mole}^{-2}$ and $b = 0.03913 \text{ L mole}^{-1}$. Compare your result with that obtained using the following data: $H_m(130 \text{ K}, 1 \text{ atm}) = 10.655 \text{ kJ/mol}$, $H_m(298.15 \text{ K}, 1 \text{ atm}) = 15.586 \text{ kJ/mol}$, $H_m(130 \text{ K}, 600 \text{ atm}) = 7.305 \text{ kJ/mol}$, $S_m(130 \text{ K}, 1 \text{ atm}) = 0.16710 \text{ kJ/mol K}$, $S_m(298.15 \text{ K}, 1 \text{ atm}) = 0.19137 \text{ kJ/mol K}$, $S_m(130 \text{ K}, 600 \text{ atm}) = 0.09633 \text{ kJ/mol K}$.

First we evaluate $\Delta\mu_1 = \mu(T_f, p_i) - \mu(T_i, p_i)$, when the temperature changes from 298.15 K to T at a constant pressure of 1 atm. The plan is simple:

- Get $C_p(T, 1\text{atm})$ and $s(298.15 \text{ K}, 1 \text{ atm})$ from a database.
- Integrate $s(T, p_i) = s(T_i, p_i) + \int_{T_i}^T \frac{C_p(T, p_i)}{T} dT$ to obtain $s(T, p = 1 \text{ atm})$.
- Use the expression obtained for $s(T, p = 1 \text{ atm})$ in $\Delta\mu_1 = - \int_{T_i}^{T_f} s(T, p_i) dT$ and integrate to get $\mu(T, p = 1 \text{ atm})$.

Next, we evaluate $\Delta\mu_2 = \mu(T_f, p_f) - \mu(T_f, p_i) = \int_{p_i}^{p_f} v(T_f, p) dp$. Here we encounter a difficulty. There is no explicit expression for $v(T_f, p)$, so the integral cannot be performed directly. There is a way out of this difficulty. The variable of integration may be changed from p to v . Since the integral is performed at constant temperature, $dp = \left(\frac{\partial p}{\partial V}\right)_T dV$. Inserting this in the expression for μ gives

$$\mu(T_f, p_f) - \mu(T_f, p_i) = \int_{v(T_f, p_i)}^{v(T_f, p_f)} v(T_f, p) \left(\frac{\partial p}{\partial V}\right)_{T=T_f} dV$$

Note that when the variable of integration is changes, the limits of integration is chnged from p_i and p_f to $v(T_f, p_i)$ and $v(T_f, p_f)$. THE steps involved in the evaluation of the integral are:

- For the van der Waals equation of state and calculate $v \left(\frac{\partial p}{\partial V}\right)_{T=T_f}$.
 - For the vdW equation of state calculate the molar volumes $v(T_f, p_i)$ and $v(T_f, p_f)$. For example, to find $v(T_f, p_i)$, we have to solve the equation $p_i = f(T_f, v)$ for v . This would involve solving $p_i v^3 - (p_i b + RT_f)v^2 + av - b = 0$ for v . This equation either has three real roots or two complex and one real root. If it is the latter, the real root is the molar volume of the gas. If all the three roots are real, the lowest root is the molar volume of the liquid and the highest the molar volume of the gas. This root finding is best done with a computer using some symbolic manipulation program.
 - Perform the integral.
- The Gibbs energy of a binary mixture of species a and species b at 300 K and 10 bar is given by the following expression:

$$g = 40x_a - 60x_b + RT(x_a \ln x_a + x_b \ln x_b) + 5x_a x_b \quad [\text{kJ/mol}]$$

- For a system containing 1 mole of species a and 4 moles of species b , find ΔG_{mix} and ΔS_{mix} .

- Substitute $x_a = 1$ and $x_b = 1$ to obtain the molar volumes of pure a and b respectively.
- Write the extensive Gibbs energy

$$G = 40n_a - 60n_b + RT\left(n_a \ln \frac{n_a}{n_a + n_b} + n_b \ln \frac{n_b}{n_a + n_b}\right) + 5 \frac{n_a n_b}{n_a + n_b}$$

- The chemical potentials are determined by taking the appropriate derivative

$$\mu_a = \left(\frac{\partial G}{\partial n_a}\right)_{T, P, n_b} = 40 + RT \left(\ln \frac{n_a}{n_a + n_b}\right) + 5 \frac{n_b^2}{(n_a + n_b)^2}$$

$$\mu_b = \left(\frac{\partial G}{\partial n_b}\right)_{T, P, n_a} = -60 + RT \left(\ln \frac{n_b}{n_a + n_b}\right) + 5 \frac{n_a^2}{(n_a + n_b)^2}$$

- The Gibbs energy of mixing is

$$\Delta G_{\text{mix}} = G(n_a = 1, n_b = 4) - (1\mu_a(x_a = 1) + 4\mu_b(x_b = 1))$$

The derivative of ΔG_{mix} with respect to T gives $-\Delta S_{mix}$.

(b) If the pure species are mixed together adiabatically, do you think the temperature of the system will increase, stay the same, or decrease. Explain, stating any assumptions that you make.

From ΔG_{mix} and ΔS_{mix} we can determine ΔH_{mix} . The temperature change will +ve, -ve, or zero depending on whether the ΔH_{mix} is < 0 , > 0 , or 0 .

3. (a) Calculate the entropy of mixing 3 mol of hydrogen with 1 mol of nitrogen.

This was discussed in class. $x_{N_2} = 0.25$ and $x_{H_2} = 0.75$

$$\Delta S_{mix} = nR \sum_i x_i \ln x_i$$

(b) Calculate the Gibbs energy of mixing at 25 °C.

$$\Delta G_{mix} = -T\Delta S_{mix} = -nRT \sum_i x_i \ln x_i$$

(c) At 25 °C, calculate the Gibbs energy of mixing $1 - \xi$ mol of nitrogen, $3(1 - \xi)$ mol of hydrogen, and 2ξ mol of ammonia as a function of ξ . Plot the values from $\xi = 0$ to $\xi = 1$ at intervals of 0.2

Evaluate

$$\Delta G_{mix} = -T\Delta S_{mix} = -nRT \sum_i x_i \ln x_i,$$

where $\xi_{N_2} = \frac{1-\xi}{4-2\xi}$, $\xi_{H_2} = \frac{3-3\xi}{4-2\xi}$, and $\xi_{NH_3} = \frac{2\xi}{4-2\xi}$ at intervals of 0.2 for ξ .

(d) If $\Delta G_f^\circ(NH_3) = -16.5$ kJ/mol at 25 °C, calculate the Gibbs energy of the mixture for values of $\xi = 0$ to $\xi = 1$ at intervals of 0.2. Plot G versus ξ if the initial state is the mixture of 1 mol N_2 and 3 mol of H_2 . (e) Calculate G for ξ_e at $p = 1$ atm.

This requires you to compute the Gibbs energy of the mixture, which means that

$$G = \sum_i n_i \mu_i = \sum_i n_i \left(\mu_i^\circ + RT \ln \frac{p_i}{p^\circ} \right)$$

Note that $\mu_{H_2}^\circ = \mu_{N_2}^\circ = 0$ and $n_i = x_i n$.

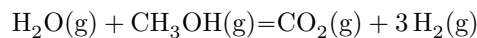
4. The reaction $SO_2(g) + \frac{1}{2}O_2 \longrightarrow SO_3$ is performed starting with 1.2 moles of SO_2 , 0.8 mole of O_2 , and 0.07 moles of SO_3 . At some time after you start the reaction, the extent of reaction is $\xi = 0.5$. Calculate the number of moles and the mole fractions of each component at that time.

$$n(SO_2; \xi = 0.5) = 1.2 + (-1).5 = 0.7$$

$$n(O_2; \xi = 0.5) = 0.8 + (-1/2).5 = 0.55$$

$$n(SO_3; \xi = 0.5) = 0.07 + (1).5 = 0.57$$

5. Fuel cells provide an attractive alternative energy source. They require an H_2 feed stream to operate. Consider a fuel cell based on the direct conversion of methanol to form hydrogen:



The reaction is carried out at 60 °C and low pressure, with a feed of twice as much water as methanol. The equilibrium extent of reaction is $\xi = 0.87$. How many moles of H_2 can be produced per mole of CH_3OH in the feed? What is the mole fraction of H_2 ?

$$n(CH_3OH; \xi = 0.87) = 1 - \xi$$

$$n(H_2O; \xi = 0.87) = 2 - \xi$$

$$n(CO_2; \xi = 0.87) = \xi$$

$$n(H_2; \xi = 0.87) = 3\xi = 2.61 \text{ moles}$$

$$x(H_2) = \frac{2.61}{3 + 2\xi} = 0.55$$

6. Calculate the equilibrium constant at 298 K for the reaction of problem 5.

$$\Delta g_{rxn.,298}^\circ = \sum \nu_i (\Delta g_f^\circ)_i = -3.83 \text{ kJ/mol}$$

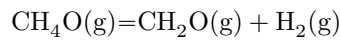
$$K = \exp\left(-\frac{\Delta g_{rxn.,298}^\circ}{RT}\right) = 4.69$$

7. Calculate the equilibrium constant at 60 °C for the reaction of problem 5.

$$\ln \frac{K_{333}}{4.69} = -\frac{48970}{8.314} \left(\frac{1}{333} - \frac{1}{298} \right) = 2.08$$

$$K_{333} = 37.44$$

8. We wish to produce formaldehyde, CH₂O, by the gas-phase pyrolysis of methanol, CH₃OH, according to:



The relevant thermochemical data is

	CH ₃ O	CH ₂ O	H ₂
$\Delta g_{f,298}^\circ$	-162.0	-110.0	0
$\Delta h_{f,298}^\circ$	-200.7	-116.0	0
A_i	2.211	2.264	3.249
B_i	1.222×10^{-2}	7.022×10^{-3}	0.422×10^{-3}
C_i	-3.450×10^{-6}	-1.877×10^{-6}	
D_i			$0.0.83 \times 10^5$

I have access to data for C_P in the form $A + BT + CT^2 + DT^{-2}$. If you have C_P in some other form, that will do just fine.

(a) What is the equilibrium constant at room temperature? Would you expect an appreciable yield of product? At 25 °C, we calculate the equilibrium constant, K ,

$$K = \exp \left(-\frac{-52000}{8.314 \times 298.2} \right) = 7.644 \times 10^{-10}$$

(b) Consider the reaction at 600 °C and 1 bar. What is the equilibrium constant (i) assuming $\Delta H_{\text{rxn}}^\circ = \text{constant}$?

$$\Delta h_{\text{rxn}}^\circ = 84.7 \text{ kJ/mol}$$

$$\ln \frac{K_{873}}{K_{298}} = -\frac{84700}{8.314} \left(\frac{1}{873} - \frac{1}{298} \right) = 22.5$$

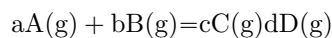
$$K_T = 4.63$$

(ii) using $\Delta H_{\text{rxn}}^\circ = \Delta H_{\text{rxn}}^\circ(T)$?

$$\ln \frac{K_{873}}{7.64 \times 10^{-10}} = 23.2$$

$$K_T = 8.67$$

9. Consider the following general gas-phase reaction:



The constant-pressure reactor also contains an inert species, I . Describe how the following reactor conditions affect yield of reaction products:

We note that

$$K = \prod_i x_i^{\nu_i} P^{\nu_i} = \frac{\left(\frac{n_C}{n_T} \right)^c \left(\frac{n_D}{n_T} \right)^d}{\left(\frac{n_A}{n_T} \right)^a \left(\frac{n_B}{n_T} \right)^b} P^v,$$

where $v = c + d - a - b$ and $n_T = n_A + n_B + n_C + n_D + n_I$. Rearranging, we have

$$K = \left[\frac{P^v}{n_T^v} \right] \frac{n_C^c n_D^d}{n_A^a n_B^b}$$

(a) temperature;

In an exothermic reaction, K decreases as temperature increases; therefore, the right-hand side must also decrease. The equilibrium will shift to the left, decreasing n_C and n_D while increasing n_A and n_B . Thus, the equilibrium conversion and potential product yield will decrease. Conversely, the equilibrium conversion of an endothermic reaction increases with increasing temperature.

(b) pressure;

Pressure is primarily affected by the term P^v . K is independent of pressure.

$$\frac{1}{P^v} = \left[\frac{1}{K n_T^v} \right] \frac{n_C^c n_D^d}{n_A^a n_B^b}$$

The effect of pressure will primarily depend on the sign of v . If the number of moles of products is greater than the number of moles of reactants, v is positive. In this case, using an argument similar to that in part (a), an increase in pressure decreases the equilibrium conversion. Conversely, if there are more reactants than products, conversion increases with increasing pressure. This is a restatement of Le Chatelier's principle.

(c) addition of inert species;

$$n_T^v = \left[\frac{P^v}{K} \right] \frac{n_C^c n_D^d}{n_A^a n_B^b}$$

If there are more moles of products than of reactants ($v > 0$), an increase of inert increases the equilibrium conversion. Conversely, if there are more moles of reactants than of products, conversion decreases with added inerts. If the moles of reactants equal the moles of products, there is no effect of adding inerts.

This effect can be understood on a molecular scale. If we consider a reaction with more moles of products than of reactants, more individual species must collide (find each other) for the reaction to proceed backward as compared to forward. Addition of an inert then makes it harder for the backward reaction relative to the forward reaction, since the inerts make it harder for the greater number of product species to find each other. Thus, the forward reaction will be greater than the reverse reaction relative to the case of no inert, and equilibrium conversion will be greater.

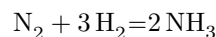
(d) additional (nonstoichiometric) reactant in feed.

If there is a reactant in the feed, the denominator on the right-hand side of requires more conversion to satisfy the equation

$$K = \left[\frac{P^v}{n_T^v} \right] \frac{n_C^c n_D^d}{n_A^a n_B^b}.$$

Thus, a reactant in the feed will increase the conversion of the other (limiting) reactant.

10. Consider the production of ammonia from the catalytic reaction of a stoichiometric feed of nitrogen and hydrogen. The reaction temperature is 500 °C and the reactor pressure is 1 bar.



What is the maximum possible conversion?

Species	ν_i	Δh_f°	Δg_f°	A_i	B_i	D_i
NH ₃	2	-46.11 kJ/mol	-16.45 kJ/mol	3.578	3.020×10^{-3}	-0.186×10^5
N ₂	-1	0	0	3.280	0.593×10^{-3}	0.040×10^5
H ₂	-3	0	0	3.578	0.422×10^{-3}	0.083×10^5

At 25 °C, we calculate the equilibrium constant, K ,

$$K = \frac{\left(\frac{2\xi}{4-2\xi} \right)^2}{\left(\frac{1-\xi}{4-2\xi} \right) \left(\frac{3-3\xi}{4-2\xi} \right)^3} P^{-2} = \exp \left(-\frac{-32900}{8.314 \times 298.2} \right) = 5.81 \times 10^5$$

(a) Take $\Delta H_{\text{rxn}}^\circ = \text{constant}$.

We use the equation

$$\ln \frac{K}{K_{298}} = \frac{\Delta h_{\text{rxn}}}{R} \left(\frac{1}{T} - \frac{1}{298} \right) = \frac{92220}{8.314} \left(\frac{1}{773} - \frac{1}{298} \right) = -22.28$$

$$K_T = 6.754 \times 10^{-5}$$

With $P = 1$ bar, the extent of the reaction is $\xi_e = 0.005$.

(b) Take $\Delta H_{\text{rxn}}^\circ = \Delta H_{\text{rxn}}^\circ(T)$.

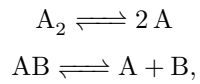
We use the equation

$$\ln \frac{K}{K_{298}} = -24.37$$

$$K_T = 1.51 \times 10^{-5}$$

With $P = 1$ bar, the extent of the reaction is $\xi_e = 0.003$.

11. Consider the two equilibria,



and assume that the $\Delta_r G^\circ$ and therefore K is the same for both. Show that the equilibrium value of ξ_2 is greater than the equilibrium value of ξ_1 ? What is the physical reason for this result?

This is straightforwardly proved.

If an enclosure at high temperature contains equal number of atoms A and B, then, when the temperature is lowered, and molecules A_2 , AB , B_2 form, they do not form in equal numbers, but in the ratio 1:2:1.

If two socks are chosen from a box containing equal number of white and black socks, the probability that a pair of black socks are chosen is $1/4$, a pair of white, $1/4$, and one black and one white, $1/2$.