

Chemistry 230
Problem Set # 8 -- Answers

1. For $\text{NH}_3(\text{g})$, $H_{\text{m},298}^\circ = H_{\text{f},298}^\circ$, since $H_{\text{m},298}^\circ = 0$ for both $\text{H}_2(\text{g})$ and $\text{N}_2(\text{g})$.

Thus $H_{\text{m},298}^\circ = -46.11 \text{ kJ/mol}$.

$S_{\text{m},298}^\circ = 192.45 \text{ J mol}^{-1} \text{ K}^{-1}$ (from Appendix).

$G_{\text{m},298}^\circ = H_{\text{m},298}^\circ - 298.15 S_{\text{m},298}^\circ = -103.489 \text{ kJ/mol}$.

$$H_{\text{m},325}^\circ = H_{\text{m},298}^\circ + \int_{298}^{325} C_{\text{P,m}}^\circ dT \quad H_{\text{m},298}^\circ + C_{\text{P,m},298}^\circ (325 - 298.15) = -45.169 \text{ kJ/mol}.$$

$$S_{\text{m},325}^\circ = S_{\text{m},298}^\circ + \int_{298}^{325} \frac{C_{\text{P,m}}^\circ}{T} dT = 195.473 \text{ J mol}^{-1} \text{ K}^{-1}.$$

$$\mu_{325}^\circ \quad G_{\text{m},325}^\circ = -108.698 \text{ kJ/mol} \quad \mu(T,P) = \mu_T^\circ + RT \ln(P/P^\circ) = -106.065 \text{ kJ/mol}.$$

2. (a) Use the equation for $H^\circ(T)$ given on p. 147 in Eq. (6.37), and integrate:

$$2R \ln \frac{K_P^\circ(T)}{K_P^\circ(298)} = A' \frac{1}{298.15 \text{ K}} - \frac{1}{T} + D \ln \frac{T}{298.15 \text{ K}} + E (T - 298.15 \text{ K}) + \frac{F}{2} \frac{1}{298.15^2 \text{ K}^2} - \frac{1}{T^2}$$

$A' = -571.528 \text{ kJ/mol}$; $D = 1.51 \text{ J mol}^{-1} \text{ K}^{-1}$; $E = 2.85 \times 10^{-3} \text{ J mol}^{-1} \text{ K}^{-2}$; $F = 1448 \text{ kJ mol}^{-1} \text{ K}$.

(b) $\ln K_P^\circ(298) = 103.74909$ $\ln K_P^\circ(1500) = 12.2098$ $K_P^\circ(1500) = 2.01 \times 10^5$.

3. $\text{A}(\text{g}) \rightleftharpoons 2 \text{B}(\text{g})$ At equilibrium we have $n_0(1-x)$ mol A and $2x n_0$ mol B

$$K_P^\circ = \frac{2x^2}{1-x} \frac{1+x}{1-x} \frac{P}{P^\circ} \quad \text{Solve for } x: \quad x = \frac{K_P^\circ}{4(P/P^\circ) + K_P^\circ}^{1/2}$$

Increasing T increases x , while increasing P decreases x .

4. $\text{A}(\text{g}) \rightleftharpoons \text{B}(\text{g}) + \text{C}(\text{g})$ At equilibrium we have $n_0(1-x)$ mol A and $x n_0$ mol of each of B and C.

$$K_P^\circ = \frac{x^2}{1-x} \frac{1+x}{1-x} \frac{P}{P^\circ} = \frac{x^2}{1-x} \frac{P}{P^\circ} = \frac{K_P^\circ}{(P/P^\circ) + K_P^\circ}^{1/2}$$

$H_{298}^\circ = 87.9 \text{ kJ/mol}$; $S_{298}^\circ = 170.266 \text{ J mol}^{-1} \text{ K}^{-1}$;

$H_{500}^\circ = 86.48 \text{ kJ/mol}$; $S_{500}^\circ = 166.620 \text{ J mol}^{-1} \text{ K}^{-1}$ $G_{500}^\circ = 3.17 \text{ kJ/mol}$ $K_P^\circ = 0.467$.

(a) At fixed $P = 0.900 \text{ bar}$, $x = 0.584$.

(b) Now $P = P_0(1-x)$, where P_0 is the initial P . Thus $K_P^\circ = \frac{x^2}{1-x} \frac{P_0}{P^\circ} = 0.506$.

5. (d) $G_{500}^\circ = 9.69 \text{ kJ/mol}$ $K_P^\circ = e^{-2.33086} = 0.09721$.

$$27 K_P^\circ = \frac{x^2 (2-x)^2}{(1-x)^4} = 0.3822 \text{ (trial \& error)}$$

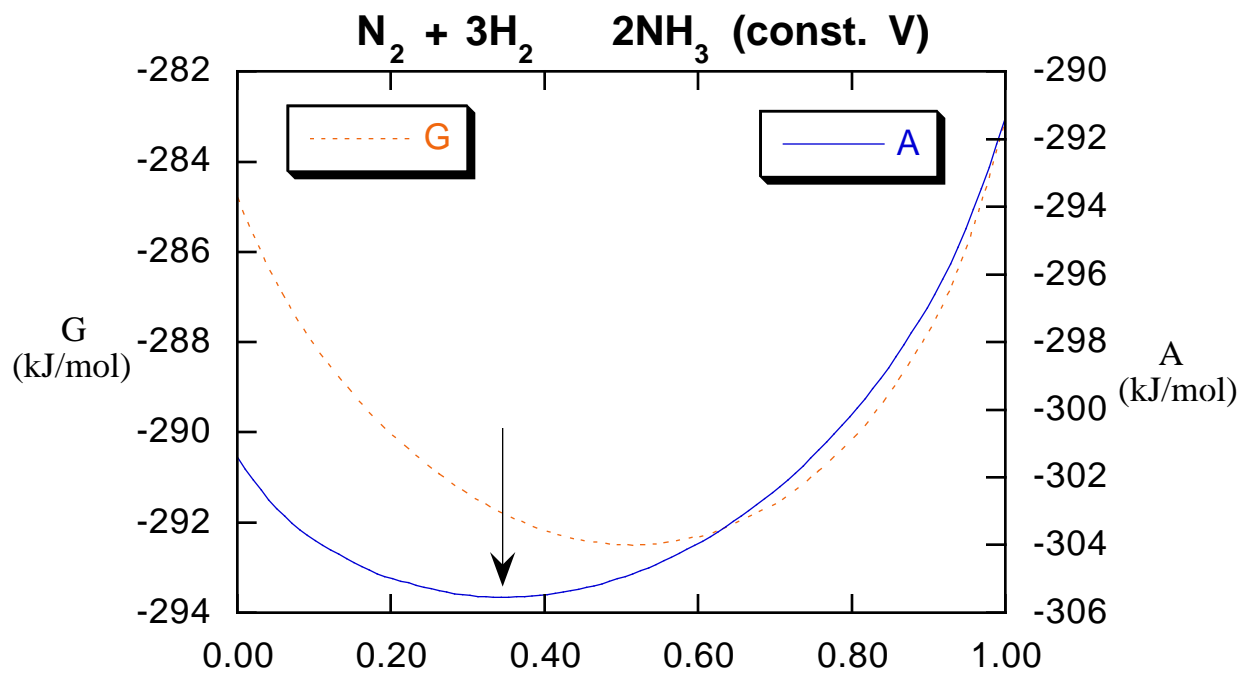
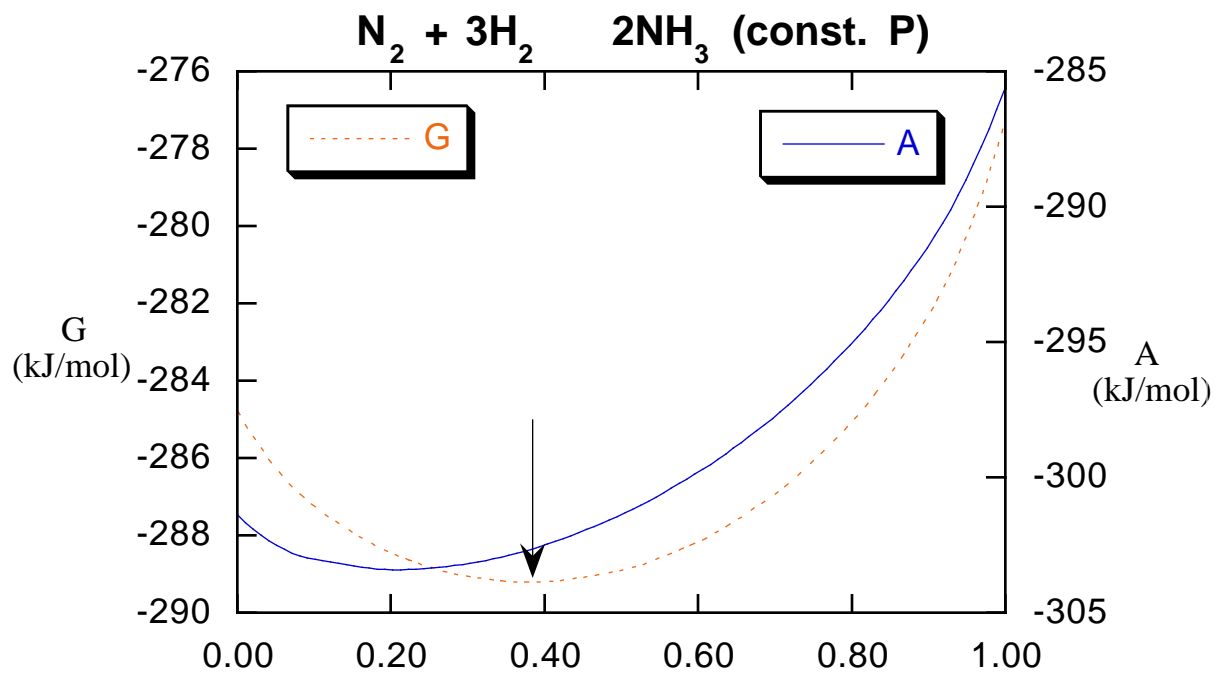
P 's(bar): N_2 — 0.764; H_2 — 2.292; NH_3 — 0.945.

(e) [See plots.]

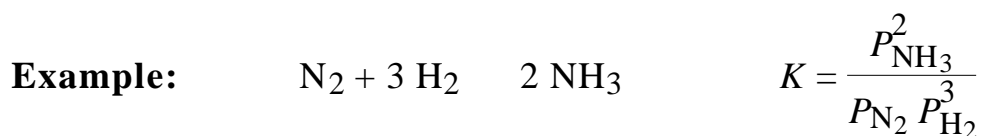
6. (a) Now $P_{\text{tot}} = (4-2x)P^\circ$ P s(bar): N_2 — $(1-x)$; H_2 — $(3-3x)$; NH_3 — $2x$.

(b) $A = G - PV = G - n_{\text{tot}}RT = \sum \mu_i n_i - (4-2x)RT$

(d) $27 K_P^\circ = \frac{4x^2}{(1-x)^4} = 0.3462$ P 's(bar): N_2 — 0.654; H_2 — 1.962; NH_3 — 0.692.



Solution of Equilibrium Problems



Start with Example 8-4, p 289. Using the ideal gas law we obtain the three given initial pressures, and hence $Q = \frac{(22)^2}{(55)(11)^3} = 6.6 \times 10^{-3}$. Since this $Q > K = 1.9 \times 10^{-4}$, the reaction will proceed from right to left. Let us now solve for the equilibrium state, using trial-and-error substitution into the expression for Q . First express Q as follows:

$$Q = \frac{(22-2x)^2}{(55+x)(11+3x)^3}, \text{ in which we take account of the reaction stoichiometry.}$$

Next we simply substitute for x in trial-and-error fashion:

x	Q
2	1.157×10^{-3}
3	5.517×10^{-4}
4	2.73×10^{-4}
5	1.365×10^{-4}
4.5	1.931×10^{-4}
4.6	1.802×10^{-4}
4.52	1.904×10^{-4}

Thus, at equilibrium, $P_{\text{NH}_3} = 12.96$, $P_{\text{N}_2} = 59.52$, and $P_{\text{H}_2} = 24.56$. Now let us decrease V by a factor of 2. Now $Q = K/4$, so the reaction must proceed to the right. The new equation we must solve is

$$K = \frac{(25.92+2x)^2}{(119.04-x)(49.12-3x)^3}$$

x	Q
1	6.73×10^{-5}
2	9.54×10^{-5}
4	1.955×10^{-4}
3.9	1.885×10^{-4}
3.92	1.899×10^{-4}

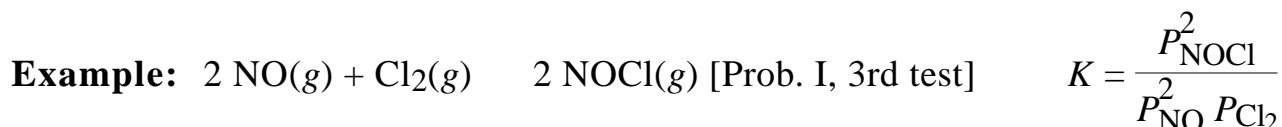
The new equilibrium P s are $P_{\text{NH}_3} = 33.76$, $P_{\text{N}_2} = 115.12$, $P_{\text{H}_2} = 37.36$. Now let us see what happens when we add some H_2 to the equilibrium mix at the end of the first calculation. Let us increase the pressure of H_2 by 5.00 atm. This will drive the reaction toward the right, and the equation we must solve is

$$K = \frac{(12.96+2x)^2}{(59.52-x)(29.56-3x)^3}$$

x	Q
2	3.82×10^{-4}
1	2.04×10^{-4}
0.8	1.802×10^{-4}
0.88	1.894×10^{-4}
0.89	1.906×10^{-4}

Thus the final P s in this case are $P_{\text{NH}_3} = 14.74$, $P_{\text{N}_2} = 58.63$, $P_{\text{H}_2} = 26.89$.

More on Solution of Equilibrium Problems



In part F we find that $Q = \frac{(2)^2}{(2)^2(2)} = 0.5$. Since this $Q < K = 2.73$, the reaction will proceed from left to right. As before let us solve for the equilibrium state, using trial-and-error substitution into the expression for Q . First express Q as follows:

$$Q(x) = \frac{(2+2x)^2}{(2-2x)^2 (2-x)}, \text{ in which we take account of the reaction stoichiometry.}$$

Next we substitute for x in trial-and-error fashion:

x	Q
0.5	6.00
0.4	3.403
0.3	2.029
0.35	2.614
0.36	2.753
0.358	2.725
0.359	2.739
0.3583	2.7292
0.3584	2.7306

We know that the gas pressures are convertible to concentrations through the ideal gas law: $c = [] = \frac{n}{V} = \frac{P}{RT}$. Thus, at equilibrium, we have the following pressures and concentrations:

	$P(\text{atm})$	$[] (\text{mol/L})$
NO	1.283	0.02728
Cl ₂	1.642	0.03490
NOCl	2.717	0.05776

Substitution of these P 's back into the expression for K above verifies that this is

indeed an equilibrium state. Furthermore, if we substitute these **concentrations** into the equivalent expression for the concentration equilibrium constant,

$$K_c = \frac{[\text{NOCl}]^2}{[\text{NO}]^2 [\text{Cl}_2]},$$

we obtain a numerical value of 128.4, in agreement with the answer to part E, which we obtained using the relation,

$$K_c = K (RTc^\circ/P^\circ)^{-n}.$$

Thus we see that the concentration and pressure equilibrium laws provide an **equivalent** description of the reaction: Had we started with

$$Q_c(y) = \frac{(a+2y)^2}{(a-2y)^2 (a-y)},$$

where $a = (2 \text{ atm}/RT) = 0.04252 \text{ mol/L}$, and solved for the value of y needed to yield $Q_c(y) = K_c = 128.4$, we would have obtained **directly** the concentrations obtained above by simply converting the equilibrium P s for the three substances.

Note: In all these calculations, the reference P° was 1.00 atm instead of 1.00 bar. You can easily convert the K_P° values to the 1.00 bar reference state by converting the equilibrium P values in atm to bar and then just recomputing the equilibrium expression. On the other hand the K_c° values do not require correction. (Why not?)