Chem 322: Physical Chemistry II

Spring 2025 Exam 3
Professor Yuting Chen

Name: ______________________________

This is an open note exam. You may use your prepared two-page cheat sheet and calculator, but no other external resources. No other electronics may be in your possession. The Hamilton College Honor Code applies to this exam.

By my signature below, I affirm on my honor the work represented in this exam is solely my own, and that I did not give or receive assistance on this exam. Violating the Honor Code will result in automatic failure of the course.

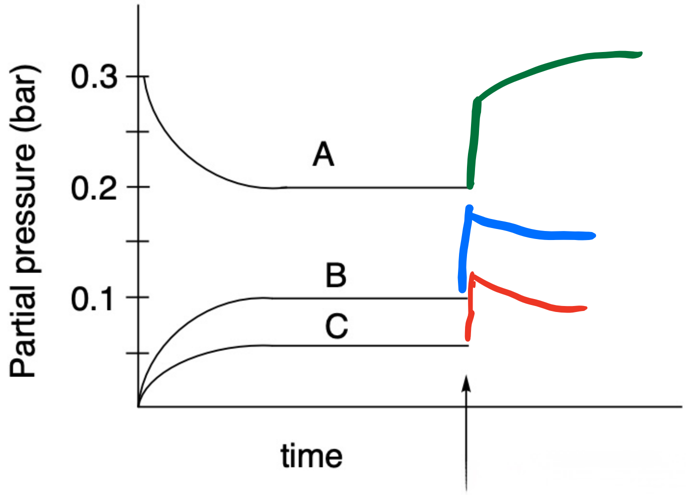
Signature: ______________________________

Instructions

- Do not turn the page until instructed. You have 4 hours for the exam.
- Ensure you have all pages of the exam. The exam consists of one cover page and 7 pages of questions.
- Write your answers in the spaces indicated. Anything written on the backs of pages will not be graded. If you need more space, ask for scratch paper.
- Write legibly and show all of your work clearly and logically. Even if the final answer is correct, you may not receive credit if your work is incomplete, indecipherable, or unable to be followed.
- Grading is based on the consistency of your work. If you make an error in one step, you may still receive credit for later steps if your other steps are consistent, so it is in your best interest to attempt all parts of a problem.
- Include units for all of your answers. Report answers with a reasonable number of significant figures unless otherwise specified.

1. **Equilibrium Response to Stressors**

Use the figure showing the partial pressures of three ideal gases at standard conditions to answer the following questions.



(a) (2 points) Write the balanced chemical equation for the equilibrium, including all phases.

$$2\,A(g) \rightleftharpoons 2\,B(g) + C(g)$$

(b) (6 points) Use the data to calculate K_c and K.

$$K = \frac{(0.10)^2(0.05)}{(0.20)^2}$$
$$= \boxed{0.0125}$$
$$K = \left(\frac{c^\circ RT}{P^\circ}\right) K_c$$
$$K_c = \frac{K}{\left(\frac{c^\circ RT}{P^\circ}\right)}$$
$$K_c = \frac{0.0125}{\left(\frac{(1\,\frac{\text{mol}}{\text{L}})(0.083\,14\,\frac{\text{L}\cdot\text{bar}}{\text{mol}\cdot\text{K}})(298\,\text{K})}{1\,\text{bar}}\right)}$$
$$= \boxed{5.04 \times 10^{-4}}$$

(c) (4 points) The system at equilibrium is isothermally compressed at the point indicated by the arrow. Sketch the qualitative changes in partial pressures immediately after compression and at the new equilibrium.

2. **Hess's Law**

Consider the following equilibrium at standard conditions:

$$\mathrm{CS_2(g) + H_2O\,(g) + H_2(g) \rightleftharpoons CO\,(g) + 2\,H_2S\,(g)} \quad K_c = 100$$
$$\frac{1}{2}\,\mathrm{CS_2(g) + 2\,H_2(g)} \rightleftharpoons \frac{1}{2}\,\mathrm{CH_4(g) + H_2S\,(g)} \quad K_c = 20$$

(a) (4 points) Combine the two equilibria to make a target equilibrium that has 1 mol $CO\,(g)$ as a product and has eliminated $H_2S\,(g)$ from the equilibrium. Write the resulting equilibrium reaction and calculate the corresponding equilibrium constant K_c.

$$\mathrm{CS_2(g) + H_2O\,(g) + H_2(g) \rightleftharpoons CO\,(g) + 2\,H_2S\,(g)} \quad K_c = 100$$
$$\mathrm{CH_4(g) + 2\,H_2S\,(g) \rightleftharpoons CS_2(g) + 4\,H_2(g)} \quad K_c = \frac{1}{20^2}$$
$$\mathrm{CH_4(g) + H_2O\,(g) \rightleftharpoons CO\,(g) + 3\,H_2(g)} \quad \boxed{K_c = 0.25}$$

(b) (8 points) The system is initially setup with $P_{CO} = 2\,\mathrm{atm}$, $P_{H_2} = 2\,\mathrm{atm}$, $P_{CH_4} = 4\,\mathrm{atm}$ and $P_{H_2O} = 3\,\mathrm{atm}$. Based on the given initial pressures, determine the direction in which the equilibrium will shift and justify your reasoning.

$$\begin{aligned}
Q &= \frac{P_{CO}(P_{H_2})^3}{P_{CH_4}P_{H_2O}} \\
&= \frac{(2\cdot 1.01325)\,(2\cdot 1.01325)^3}{(4\cdot 1.01325)(3\cdot 1.01325)} \\
Q &= 1.37 \\
\Delta n &= (1+3)-(1+1) = 2 \\
K &= \left(\frac{c^\circ RT}{P^\circ}\right)^{\Delta n} K_c \\
&= \left(\frac{(1\,\frac{\mathrm{mol}}{\mathrm{L}})(0.083\,14\,\frac{\mathrm{L\cdot bar}}{\mathrm{mol\cdot K}})(298\,\mathrm{K})}{1\,\mathrm{bar}}\right)^2 (0.25) \\
&= 153.5 \\
Q &< K \implies \boxed{\text{Shift towards products}}
\end{aligned}$$

3. **Solubility**

(a) (2 points) AgBr has a $K_{sp} = 5.35 \times 10^{-13}$ at 25 °C. Write the equilibrium expression corresponding to this K_{sp} value.

$$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$$

(b) (3 points) A silver cation forms a complex with ammonia in water according to the following equilibrium:

$$Ag^+(aq) + 2\,NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq) \qquad K = 1.1 \times 10^7$$

What is the value of the equilibrium constant, K, for the following reaction?

$$AgBr(s) + 2\,NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq) + Br^-(aq)$$

$$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq) \qquad K_{sp} = 5.35 \times 10^{-13}$$

$$Ag^+ + 2\,NH_3 \rightleftharpoons [Ag(NH_3)_2]^+ \qquad K = 1.1 \times 10^7$$

$$AgBr(s) + 2\,NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq) + Br^-(aq) \qquad K_{eq} = K_{sp} \cdot K$$

$$K_{eq} = (5.35 \times 10^{-13})(1.1 \times 10^7)$$

$$= \boxed{5.89 \times 10^{-6}}$$

(c) (10 points) Find the concentration of each $NH_3(aq)$ and $Br^-(aq)$ at equilibrium when an excess of AgBr(s) is added to 250.0 mL of a 0.020 M aqueous solution of NH_3.

	Ag^+	NH_3
I	0	0.020
C	$+x$	$-2x$
E	x	$0.020 - 2x$

$$K = \frac{[Ag(NH_3)_2{}^+][Br^-]}{[NH_3]^2}$$

$$5.89 \times 10^{-6} = \frac{x^2}{(0.020 - 2x)^2} =$$

$$\frac{x}{0.020 - 2x} = 2.426 \times 10^{-3}$$

$$x = \boxed{4.85 \times 10^{-5} = [Br^-]}$$

$$[NH_3] = 0.02 - 2x = \boxed{1.99 \times 10^{-2}}$$

(d) (4 points) Consider the following system at equilibrium (EQ1):

$$Ag^+(aq) + 2\,NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq)$$

NH_3 is added to this system. *Immediately*, what is the impact on these variables. Fill in $<$, $>$, $=$ or X for cannot be determined.

(e) (2 points) Q ___$<$___ K

(f) (2 points) ΔG_{toeq} ___$<$___ 0

A new equilibrium (EQ2) is established. Compare the following quantities:

(g) (2 points) mol Ag^+ @ EQ1 ___$>$___ mol Ag^+ @ EQ2

(h) (2 points) $[NH_3(aq)]$ @ EQ1 ___$<$___ $[NH_3(aq)]$ @ EQ2

(i) (2 points) ΔG_T @ EQ1 ___$=$___ ΔG_T @ EQ2

(j) (2 points) pH @ EQ1 ___$<$___ pH @ EQ2

(k) (2 points) Q @ EQ1 ___$=$___ K @ EQ2

(l) (3 points) Adding water to the system at equilibrium will: (Circle all that apply)

A. Immediately make $Q < K$

B. Result in more $[Ag(NH_3)_2]^+(aq)$ at equilibrium

C. Result in more mols of NH_3 at equilibrium

4. **Equilibrium**

Consider the equilibrium:

$$2\,COF_2(g) \rightleftharpoons CO_2(g) + CF_4(g) \quad K = 4$$

(a) (10 points) Calculate the temperature at which the given equilibrium constant K was determined, using the data provided.

	ΔH_f° ($\frac{kJ}{mol}$)	S_m° ($\frac{J}{mol \cdot K}$)
$CO_2(g)$	−393.5	213.8
$COF_2(g)$	−638.0	258.88
$CF_4(g)$	−933.6	261.6

Use table values to solve for thermodynamic quantities:

$$\begin{aligned}\Delta H^\circ &= [-393.5\,\tfrac{kJ}{mol} + -933.6\,\tfrac{kJ}{mol}] - 2[-638.0\,\tfrac{kJ}{mol}] \\ &= -51.1\,\tfrac{kJ}{mol} \\ &= -51\,100\,\tfrac{J}{mol} \\ \Delta S^\circ &= [213.8\,\tfrac{J}{mol \cdot K} + 261.6\,\tfrac{J}{mol \cdot K}] - 2[258.88\,\tfrac{J}{mol \cdot K}] \\ &= -42.36\,\tfrac{J}{mol \cdot K}\end{aligned}$$

Use gibbs relation to solve for T:

$$\begin{aligned}\Delta H^\circ - T\Delta S^\circ &= -RT\ln K \\ -51\,100\,\tfrac{J}{mol} + T(42.36\,\tfrac{J}{mol \cdot K}) &= -(8.314\,\tfrac{J}{mol \cdot K})(T)\ln(4) \\ -51\,100\,\tfrac{J}{mol} &= -T(53.88\,\tfrac{J}{mol \cdot K}) \\ T &= \frac{51\,100\,\frac{J}{mol}}{53.88\,\frac{J}{mol \cdot K}} \\ &= \boxed{948\,K}\end{aligned}$$

(b) (10 points) A constant pressure vessel contains an initial partial pressure of $COF_2(g)$ of 1.50 bar, an unknown initial partial pressure of $CO_2(g)$, and an initial partial pressure of $CF_4(g)$ of 0.255 bar. At equilibrium, the partial pressure of $COF_2(g)$ is 0.49 bar.

Determine the equilibrium partial pressures of $CF_4(g)$ and $CO_2(g)$, and calculate the initial partial pressure of $CO_2(g)$.

	COF_2	CO_2	CF_4
I	1.5	y	0.255
C	-2x	$+x$	$+x$
E	0.49	$y + x$	0.255 + x

Solve for x

$$\begin{aligned} 1.50\,\text{bar} - 2x &= 0.49\,\text{bar} \\ 2x &= 1.01\,\text{bar} \\ x &= 0.505\,\text{bar} \end{aligned}$$

Plug into K expression:

$$\begin{aligned} P_{CF_4} &= 0.255\,\text{bar} + 0.505\,\text{bar} = 0.760\,\text{bar} \\ K &= \frac{P_{CO_2} P_{CF_4}}{(P_{COF_2})^2} \\ 4 &= \frac{(y + 0.505)(0.760)}{(0.49)^2} \\ y + 0.505 &= 1.264\,\text{bar} \\ y &= 0.759\,\text{bar} \end{aligned}$$

$$\boxed{\begin{aligned} P_{CF_4,\,\text{eq}} &= 0.760\,\text{bar} \\ P_{CO_2,\,\text{eq}} &= 1.264\,\text{bar} \\ P_{CO_2,\,\text{initial}} &= 0.759\,\text{bar} \end{aligned}}$$

5. **Gibbs**

Consider the equilibrium:

$$2\,SO_3(g) \rightleftharpoons 2\,SO_2(g) + O_2(g)$$

1.000 mole of SO_2 and 1.000 mole of O_2 are introduced into a rigid 1.5 L flask at 750 K. When equilibrium is established, the total number of moles in the flask is found to be 1.9.

(a) (10 points) Determine ΔG_{750}

ICE table in mols:

	SO_3	SO_2	O_2
I	0	1	1
C	$+2x$	$-2x$	$-x$
E	$2x$	$1-2x$	$1-x$

At equilibrium, $2x + (1-2x) + (1-x) = 1.9 \implies x = 0.1$

$$SO_2 : 0.8\,\text{mol} \quad O_2 : 0.9\,\text{mol} \quad SO_3 : 0.2\,\text{mol}$$

Solving for K_c:

$$K_c = \frac{[SO_2]^2[O_2]}{[SO_3]^2}$$

$$K_c = \frac{\left(\frac{0.8\,\text{mol}}{1.5\,\text{L}}\right)^2 \cdot \left(\frac{0.9\,\text{mol}}{1.5\,\text{L}}\right)}{\left(\frac{0.2\,\text{mol}}{1.5\,\text{L}}\right)^2} = 9.64$$

Convert to K

$$K = \left(\frac{c^\circ RT}{P^\circ}\right)^{\Delta n} K_c = \left(\frac{(1\,\frac{\text{mol}}{\text{L}})(0.083\,14\,\frac{\text{L}\cdot\text{bar}}{\text{mol}\cdot\text{K}})(750\,\text{K})}{1\,\text{bar}}\right)^1 \cdot 9.64 = 601$$

Finally solve for ΔG_{750}:

$$\Delta G^\circ = -RT\ln K = -(8.314\,\frac{\text{J}}{\text{mol}\cdot\text{K}}) \cdot 750\,\text{K} \cdot \ln(601) = \boxed{-39.9\,\frac{\text{kJ}}{\text{mol}}}$$

(b) (4 points) Is there enough information to determine ΔG°? If there is, calculate it. If there isn't, describe the minimum amount of additional information you would need and explain how you would use it to calculate ΔG°.

No, need either K_{298} to calculate directly using $\Delta G = -RT\ln K$ or ΔH_{rxn} and use van Hoff to find K_{298} .