Chem 322: Physical Chemistry II

Spring 2026 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 5 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. **A mix of everything**

k_H of $\mathrm{CO_2}$ in water is $3.4 \times 10^{-2}\,\frac{\mathrm{mol}}{\mathrm{L \cdot bar}}$ at 298 K.

(a) (4 points) Write the K expression for this equilibrium. What is the value of the equilibrium constant K at 298K?

$$\mathrm{CO_2(g)} \rightleftharpoons \mathrm{CO_2(aq)} \qquad K = 3.4 \times 10^{-2}$$

(b) (2 points) Temperature is increased. What happens to K?

A. K increase B. K decrease C. K remains constant D. Cannot be determined

(c) (8 points) Find ΔG° for the following equilibrium given the following information.

$$\begin{array}{rl} \mathrm{CO_2(aq) + H_2O\,(l) \rightleftharpoons H_2CO_3(aq)} & \qquad \Delta G = \,? \\ \mathrm{CO_2(g) + H_2O\,(l) \rightleftharpoons H_2CO_3(aq)} & \qquad K = 15 \end{array}$$

$$\begin{array}{rl} \mathrm{CO_2(g) + H_2O\,(l) \rightleftharpoons H_2CO_3(aq)} & \qquad K_1 = 15 \\ \mathrm{CO_2(aq) \rightleftharpoons CO_2(g)} & \qquad K_2 = \dfrac{1}{3.4 \times 10^{-2}} = 29.41 \\ \hline \mathrm{CO_2(aq) + H_2O\,(l) \rightleftharpoons H_2CO_3(aq)} & \qquad K_{net} = 15 \times 29.41 = 441.15 \end{array}$$

$$\begin{aligned} \Delta G^\circ &= -RT \ln K \\ \Delta G^\circ &= -(8.314\,\tfrac{\mathrm{J}}{\mathrm{mol \cdot K}})(298\,\mathrm{K}) \ln(441.15) \\ \Delta G^\circ &= -15\,084\,\tfrac{\mathrm{J}}{\mathrm{mol}} = \boxed{-15.1\,\tfrac{\mathrm{kJ}}{\mathrm{mol}}} \end{aligned}$$

Consider the equilibrium: $\mathrm{CO_2(g) + H_2O\,(l) \rightleftharpoons H_2CO_3(aq)}$.

The system is initially setup at equilibrium (EQ1). $\mathrm{CO_2(g)}$ is added to the system. **Immediately afterwards**, but before equilibrium is reestablished, answer the following.

(d) (2 points) How does Q compare to K?

A. $Q > K$ B. $Q = K$ C. $Q < K$

After $\mathrm{CO_2(g)}$ is added, a second equilibrium (EQ2) is established. Fill in each blank with $>, <, =,$ or X for cannot be determined.

(e) (2 points) K @ EQ1 $\underline{\quad = \quad}$ K @ EQ2

(f) (2 points) $P_{\mathrm{CO_2}}$ @ EQ1 $\underline{\quad < \quad}$ $P_{\mathrm{CO_2}}$ @ EQ2

(g) (2 points) $[\mathrm{H_2CO_3}]$ @ EQ1 $\underline{\quad < \quad}$ $[\mathrm{H_2CO_3}]$ @ EQ2

(h) (2 points) mol $\mathrm{H_2O\,(l)}$ @ EQ1 $\underline{\quad > \quad}$ mol $\mathrm{H_2O\,(l)}$ @ EQ2

2. **Solution Chemistry**

(a) (12 points) The solubility of PbF_2 is $m = 2.13 \times 10^{-3}\,\frac{\text{mol}}{\text{kg}}$ at 298 K. The density of a solution of PbF_2 is $1.2\,\frac{\text{g}}{\text{mL}}$. Calculate K_{sp} of PbF_2, stating any assumptions you make.

Assume 1000 g solvent

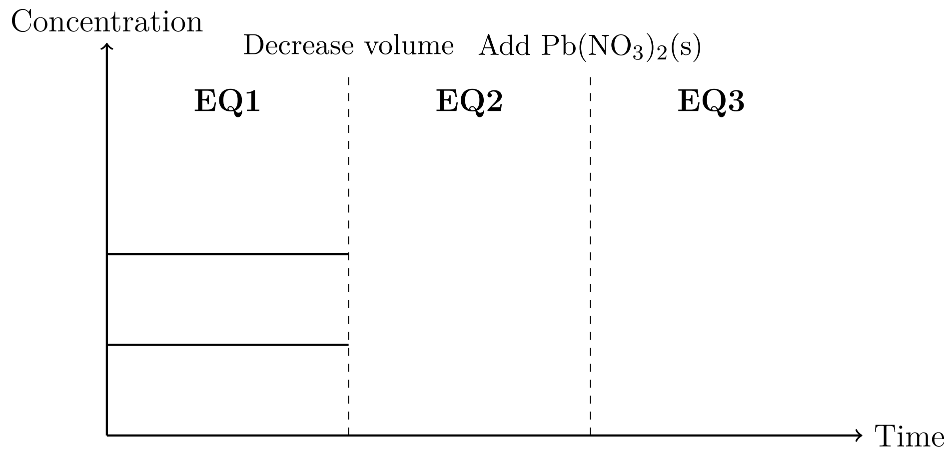
$$
\begin{aligned}
n_{\text{PbF}_2} &= (2.13 \times 10^{-3}\,\tfrac{\text{mol}}{\text{kg}})(1.000\,\text{kg}) = 2.13 \times 10^{-3}\,\text{mol} \\
m_{\text{PbF}_2} &= (2.13 \times 10^{-3}\,\text{mol})(245.2\,\tfrac{\text{g}}{\text{mol}}) = 0.5223\,\text{g} \\
m_{\text{solution}} &= 1000\,\text{g} + 0.5223\,\text{g} = 1000.52\,\text{g} \\
V_{\text{solution}} &= \frac{1000.52\,\text{g}}{1.2\,\frac{\text{g}}{\text{mL}}} = 833.77\,\text{mL} = 0.833\,77\,\text{L} \\
[\text{Pb}^{2+}] = x &= \frac{2.13 \times 10^{-3}\,\text{mol}}{0.833\,77\,\text{L}} = 2.554 \times 10^{-3}\,\tfrac{\text{mol}}{\text{L}} \\
\text{PbF}_2\text{(s)} &\rightleftharpoons \text{Pb}^{2+}\text{(aq)} + 2\,\text{F}^-\text{(aq)} \\
K_{\text{sp}} &= x(2x)^2 = 4x^3 \\
&= 4\left(2.554 \times 10^{-3}\right)^3 = \boxed{6.67 \times 10^{-8}}
\end{aligned}
$$

(b) (8 points) Calculate the molar solubility in $\frac{\text{mol}}{\text{L}}$ of PbF_2 in a solution of $0.10\,\frac{\text{mol}}{\text{L}}$ NaF.

	Pb^{2+}	F^-
I	0	0.10
C	$+x$	$+2x$
E	x	$0.10 + 2x$

$$
\begin{aligned}
\text{PbF}_2\text{(s)} &\rightleftharpoons \text{Pb}^{2+}\text{(aq)} + 2\,\text{F}^-\text{(aq)} \\
K_{\text{sp}} &= [\text{Pb}^{2+}][\text{F}^-]^2 \\
&= x(0.10 + 2x)^2 \approx x(0.10)^2 \\
x &= \frac{K_{\text{sp}}}{(0.10)^2} = \frac{6.68 \times 10^{-8}}{0.0100} \\
&= \boxed{6.68 \times 10^{-6}\,\tfrac{\text{mol}}{\text{L}}}
\end{aligned}
$$

(c) (8 points) Fill in the concentration vs time graph below for the corresponding stressors for a saturated solution of PbF_2. Be sure to label each line.



3. **Equilibrium**

2 mol of $H_2S(g)$ is added to a flexible container at 298 K, initially occupying a volume of 4 L. The system is allowed to establish equilibrium under constant pressure and temperature conditions, and the volume of the container increases by 1 L.

$$2\,H_2S(g) \rightleftharpoons 2\,H_2(g) + S_2(g)$$

(a) (10 points) Calculate K at 298 K for this equilibrium.

Hint: Think about the volume change and how it affects how you setup this problem.

	$2\,H_2S$	$2\,H_2$	S_2
I	2	0	0
C	$-2x$	$+2x$	$+x$
E	$2-2x$	$2x$	x

$$\frac{V_1}{n_1} = \frac{V_2}{n_2} \implies \frac{4}{2} = \frac{5}{2+x}$$

$$2(2+x) = 5 \implies x = 0.5\,\text{mol}$$

$$K_c = \frac{[H_2]^2[S_2]}{[H_2S]^2}$$

$$K_c = \frac{(0.2\,\text{M})^2(0.1\,\text{M})}{(0.2\,\text{M})^2}$$

$$\boxed{K_c = 0.1}$$

$$K = K_c(RT)^{\Delta n_g}$$

$$\Delta n_g = (2+1) - 2 = 1$$

$$K = 0.1 \times (0.08206 \times 298)^1$$

$$\boxed{K = 2.45}$$

(b) (6 points) It is reported that $K_{398} = 6.7$. Calculate $\Delta H^\circ_{\text{rxn}}$.

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\Delta H^\circ_{\text{rxn}} = R \cdot \ln\left(\frac{K_2}{K_1}\right)\left(\frac{1}{T_1} - \frac{1}{T_2}\right)^{-1}$$

$$= (8.314\,\tfrac{\text{J}}{\text{mol}\cdot\text{K}}) \cdot \ln\left(\frac{6.7}{2.45}\right)\left(\frac{1}{298\,\text{K}} - \frac{1}{398\,\text{K}}\right)^{-1}$$

$$= 9913.8\,\tfrac{\text{J}}{\text{mol}} = \boxed{9.91\,\tfrac{\text{kJ}}{\text{mol}}}$$

4. **Maxwell Relations**

(a) (8 points) Starting from a cyclic triple product rule and using $C_V = T\left(\frac{\partial S}{\partial T}\right)_V$, show:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\frac{T}{C_V}\left(\frac{\partial S}{\partial V}\right)_T$$

Triple product rule on T, V, S:

$$\left(\frac{\partial T}{\partial V}\right)_S \left(\frac{\partial V}{\partial S}\right)_T \left(\frac{\partial S}{\partial T}\right)_V = -1$$

Solve and invert $\left(\frac{\partial V}{\partial S}\right)_T$:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\frac{\left(\frac{\partial S}{\partial V}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_V}$$

Substitute C_V/T and the Helmholtz Maxwell relation $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$:

$$\boxed{\left(\frac{\partial T}{\partial V}\right)_S = -\frac{T}{C_V}\left(\frac{\partial P}{\partial T}\right)_V}$$

(b) (10 points) Starting from a total differential of S, show the same result. You can use $C_V = T\left(\frac{\partial S}{\partial T}\right)_V$ again.

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV = 0$$

Rearrange the terms to solve for the derivative $(\partial T/\partial V)_S$:

$$\left(\frac{\partial S}{\partial T}\right)_V dT = -\left(\frac{\partial S}{\partial V}\right)_T dV \implies \left(\frac{\partial T}{\partial V}\right)_S = -\frac{(\partial S/\partial V)_T}{(\partial S/\partial T)_V}$$

Substitute the definition $C_V = T(\partial S/\partial T)_V$ into the denominator:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\frac{(\partial S/\partial V)_T}{C_V/T}$$

Apply the Maxwell relation from $dA = -SdT - PdV$, which is $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$:

$$\boxed{\left(\frac{\partial T}{\partial V}\right)_S = -\frac{T}{C_V}\left(\frac{\partial P}{\partial T}\right)_V}$$

(c) (14 points) A gas has equation of state:

$$V = \frac{RT}{P} + aP + bT$$

where a, b are gas specific constants. Starting from $dU = T\,dS - P\,dV$, use Maxwell relations to determine constraints on a and b such that the gas behaves ideally, which is to say $\left(\frac{\partial U}{\partial P}\right)_T = 0$.

$$dU = T\,dS - P\,dV$$

Differentiate with respect to P at constant T:

$$\left(\frac{\partial U}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T - P\left(\frac{\partial V}{\partial P}\right)_T$$

Substitute Maxwell $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$:

$$\left(\frac{\partial U}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P - P\left(\frac{\partial V}{\partial P}\right)_T$$

For the given equation of state $V = \frac{RT}{P} + aP + bT$, compute the partial derivatives:

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} + b \qquad \left(\frac{\partial V}{\partial P}\right)_T = -\frac{RT}{P^2} + a$$

Substitute these derivatives back into the energy expression:

$$\begin{aligned}\left(\frac{\partial U}{\partial P}\right)_T &= -T\left(\frac{R}{P} + b\right) - P\left(-\frac{RT}{P^2} + a\right)\\ &= -\frac{RT}{P} - bT + \frac{RT}{P} - aP\\ \boxed{0 = -aP - bT} &\implies \boxed{a = -\frac{bT}{P}}\end{aligned}$$