

CHEM 103: General Chemistry II

Mid-Term Examination (100 points)

1. (5 pt each) **(a)** What is ΔG° and the value of equilibrium constant, K , at 1000 °C for the reaction, $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$? Assume that ΔH° and ΔS° are independent of temperature. [ΔH°_f : -1206.9 (CaCO₃), -635.1 (CaO), -393.5 (CO₂) kJ; S° : 92.9 (CaCO₃), 38.2 (CaO), 213.7 (CO₂) J/K]

(b) What is the temperature at which a reaction such as decomposition of CaCO₃ changes from nonspontaneous to spontaneous under standard conditions?

2. (5 pt each) Ascorbic acid (Vitamin C) is a diprotic acid, $\text{H}_2\text{C}_6\text{H}_6\text{O}_6$. The acid ionization constants are $K_{a1} = 7.9 \times 10^{-5}$ and $K_{a2} = 1.6 \times 10^{-12}$.

(a) What is the pH of a 0.1M solution?

(b) What is the concentration of ascorbate ion, $\text{C}_6\text{H}_6\text{O}_6^{2-}$?

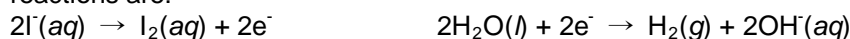
3. (5 pt each) **(a)** Calculate the equilibrium constant at 25 °C for the reaction, $\text{Zn}(\text{s}) + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu}(\text{s})$. The corresponding standard cell potential (electromotive force, emf) is 1.10 V.

(b) What is the emf at 25 °C of the following cell?

$\text{Zn}(\text{s}) \mid \text{Zn}^{2+}(0.001 \text{ M}) \parallel \text{Cu}^{2+}(10.0 \text{ M}) \mid \text{Cu}(\text{s})$

(c) What happens, when we dip a strip of copper into a solution of ZnSO₄?

(d) When an aqueous solution of potassium iodide is electrolyzed using platinum electrodes, the half-reactions are:



How many grams of iodine are produced, when a current of 8.52 mA flows through the cell for 10 min? (MW of I₂ = 254 g; R = 8.3145 J K⁻¹mol⁻¹)

4. (10 pt) When 3.0 mol O₂(g) is heated at a constant pressure of 3.25 atm, its temperature increases from 260 K to 285 K. Given that the molar heat capacity of O₂ at constant pressure is 29.4 J K⁻¹ mol⁻¹, calculate q , ΔH , and ΔE (Assume the ideal gas behavior and R = 8.3145 J K⁻¹mol⁻¹).

5. (10 pt) One mole of helium gas initially at 1.00 atm is heated, raising its temperature from 25 °C to 275 °C. Calculate ΔS in J/K assuming ideal gas behavior and (a) constant V or (b) constant P. Use the data shown in below, assumed T-independent. Note which process produces a larger ΔS , and explain briefly. Show that ΔS for the isobaric heating can also be obtained by considering a two-stage process, isochoric heating followed by isothermal expansion ($C_p = 4.968$ cal/mol K; R = 1.9872 cal/mol K).

6. (10 pt) Calculate the Gibbs free energy and entropy due to mixing 2.5 moles of Ar with 3.5 moles of oxygen, both at 1 bar and 25 °C. Assume ideal gas behavior.

7. (5 pt each) One ecologically important equilibrium is that between carbonate and hydrogencarbonate ions in natural water [$\text{CO}_3^{2-}(\text{aq}) + 3\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{HCO}_3^-(\text{aq}) + \text{H}_2(\text{g})$]. **(a)** The standard Gibbs energies for the formation of $\text{CO}_3^{2-}(\text{aq})$ and $\text{HCO}_3^-(\text{aq})$ are -527.81 and -586.77 kJ mol⁻¹, respectively. What is the standard cell voltage of the $\text{HCO}_3^-/\text{CO}_3^{2-}$ and H^+/H_2 couple? **(b)** Calculate the standard voltage of a cell in which the cell reaction is $\text{Na}_2\text{CO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{NaHCO}_3(\text{aq}) + \text{NaOH}(\text{aq})$ [standard reduction potential of the $2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$ half-reaction is -0.83 V and F = 96485 J V⁻¹ mol⁻¹].

8. (10 pt) Calculate the cell potential of the following electrochemical cell at 80 °C. Assume that ΔH is independent of temperature over the relevant temperature range [$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$ $E^\circ = 0.80$ V; $\text{I}_2 + 2\text{e}^- \rightarrow 2\text{I}^-$ $E^\circ = 0.53$ V]. $2\text{Ag}^+(\text{aq}) + 2\text{I}^- \rightarrow \text{I}_2 + 2\text{Ag}(\text{s})$ [$\Delta H = -100.0$ kJ/mol at 25 °C]

9. (5 pt each) The work done by an engine may depend on its orientation in a gravitational field. A chemical reaction takes place in a container of cross-sectional area 55.0 cm²; the container has a piston of mass 250 g at one end. As a result of the reaction, the piston is pushed out **(a)** horizontally, **(b)** vertically through 155 cm against an external pressure of 105 kPa. Calculate the work done by the system in each case. The acceleration of gravity is 9.81 m s⁻².

CHEM 103: General Chemistry II
Mid-Term Examination (100 points): Answers

1. (Total 10 pts)

(a) (5pts)

$$\Delta H^{\circ} = [(-635.1 - 393.5) - (-1206.9)]\text{kJ} = 178.3 \text{ kJ}$$

$$\Delta S^{\circ} = [(38.2 + 213.7) - (92.9)] \text{ J/K} = 159.0 \text{ J/K}$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} = 178.3 \text{ kJ} - (1273 \text{ K}) \times (0.159 \text{ kJ/K}) \rightarrow \text{Equation: 1.5 point}$$
$$= -24.1 \text{ kJ} \rightarrow \text{Answer: 1.5 pts (If unit is missing or wrong, deduct -1 point)}$$

$$\log K = \Delta G^{\circ} / (-2.303RT) = 0.989 \rightarrow \text{Equation: 1 point}$$

$$K = 9.75 \rightarrow \text{Answer: 1 point}$$

(b) (5pts)

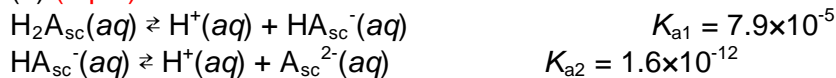
$$\Delta G^{\circ} = 0 = \Delta H^{\circ} - T\Delta S^{\circ} \rightarrow \text{Equation: 2 pts}$$

$$T = \Delta H^{\circ} / \Delta S^{\circ} = 1121 \text{ K or } (848 \text{ }^{\circ}\text{C}) \rightarrow \text{Answer: 3 pts}$$

(If unit is missing or wrong, deduct -1 point)

2. (Total 10 pts)

(a) (5 pts)



	$\text{H}_2\text{A}_{\text{sc}}(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{HA}_{\text{sc}}^-(\text{aq})$		
Starting	0.1	0	0
Change	-x	+x	+x
Equilibrium	0.1-x	x	x

$$\begin{aligned} K_{\text{a}1} &= \frac{[\text{H}^+(\text{aq})][\text{HA}_{\text{sc}}^-(\text{aq})]}{[\text{H}_2\text{A}_{\text{sc}}(\text{aq})]} = 7.9 \times 10^{-5} \\ &= \frac{x^2}{(0.1 - x)} \quad \rightarrow \text{Up to here, equation: 2 pts} \end{aligned}$$

Assuming x to be much smaller than 0.1

$$x^2/0.1 = 7.9 \times 10^{-5}$$

$$x = 0.0028 = [\text{H}^+] \quad \rightarrow \text{If obtained } [\text{H}^+] \text{ value, 1 point}$$

$$\begin{aligned} \text{pH} &= -\log[\text{H}^+] = -\log[0.0028] = \underline{2.55} \quad \rightarrow \text{Answer: 2 pts} \\ &\quad \quad \quad 1 \text{ point} \quad \quad \quad 1 \text{ point} \end{aligned}$$

(b) (5 pts)

	$\text{HA}_{\text{sc}}^-(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{A}_{\text{sc}}^{2-}(\text{aq})$		
Starting	0.0028	0.0028	0
Change	-y	+y	+y
Equilibrium	0.0028-y	0.0028+y	y

$$\begin{aligned} K_{\text{a}2} &= \frac{[\text{H}^+(\text{aq})][\text{A}_{\text{sc}}^{2-}(\text{aq})]}{[\text{HA}_{\text{sc}}^-(\text{aq})]} = 1.6 \times 10^{-12} \\ &= \frac{(0.0028 + y)y}{(0.0028 - y)} \sim 0.0028y/0.0028 = y \quad \rightarrow \text{Up to here, equation 3 pts} \end{aligned}$$

$$[\text{A}_{\text{sc}}^{2-}(\text{aq})] = \underline{1.6 \times 10^{-12}} \quad \rightarrow \text{Answer: 2 pts}$$

(In case the wrong $[\text{H}^+]$ value obtained from (a) is used in this equation, give 3 pts for ONLY right equation.)

3. (total 20pts)

(a) (5 pts)

$$\Delta G^\circ = -nFE^\circ = \text{or } -2.303RT\log K$$

$$-2 \times 96500 \times 1.10 = -2.303 \times 8.31 (\text{J/mol K}) \times 298 (\text{K}) \times \log K \rightarrow \text{Equation: 2 pts}$$

$$\log K = 37.2$$

$$K = 1.6 \times 10^{37} \rightarrow \text{Answer: 3 pts}$$

(b) (5 pts)

$$E_{\text{cell}} = E_{\text{cell}}^\circ - (0.0592/n)\log Q$$

$$Q = [\text{Zn}^{2+}]/[\text{Cu}^{2+}] = 1.0 \times 10^{-4} \rightarrow \text{Up to here: 2 pts}$$

$$E_{\text{cell}} = 1.10 - (0.0592/2)\log(1.0 \times 10^{-4})$$

$$= 1.10 - (-0.12) = 1.22 (\text{V})$$

\rightarrow Answer: 3 pts (If unit is missing or wrong, deduct -1 point)

(c) (5 pts) Nothing: The transformation ($\Delta G^\circ = 212 \text{ kJ}$, $E^\circ = -1.10 \text{ V}$) is not spontaneous.

Answer: Nothing or Not spontaneous, 5 pts;

(d) (5 pts)

$$10 \text{ min} = 6.0 \times 10^2 \text{ s}$$

$$\text{The amount of charge is } 8.52 \times 10^{-3} (\text{A}) \times 6.0 \times 10^2 (\text{sec}) = 5.11 \text{ C}$$

Two moles of electrons are equivalent to one mole of I_2 .

$$5.11 (\text{C}) \times [1 \text{ mol C} / 9.65 \times 10^4 \text{ C}] \times [1 \text{ mol } \text{I}_2 / 2 \text{ mole}] \times [254 \text{ g} / 1 \text{ mol } \text{I}_2] = 6.74 \times 10^{-3} \text{ g } \text{I}_2$$

\rightarrow Equation: 2 pts, Answer 3 pts.

(If unit is missing or wrong, deduct -1.5 point)

4. (Total 10 pts)

$$q \text{ (3.5 pts)} = C_p \Delta T = n C_{p,m} \Delta T = 3.0 \text{ mol} \times 29.4 \text{ J K}^{-1} \text{ mol}^{-1} \times 25 \text{ K} = \underline{2.2 \text{ kJ}}$$

→ Equation 1.5 pts / Answer 2 pts (Unit: -1 point)

$$\Delta H \text{ (3.5pts)} = q = \underline{2.2 \text{ kJ}} \text{ (at constant pressure)}$$

→ Equation 1.5 pts / Answer 2 pts (Unit: -1 point)

$$\Delta E \text{ (3pts)} = \Delta H - \Delta(pV) = \Delta H - \Delta(nRT) \text{ (ideal gas)}$$
$$= \Delta H - nR \Delta T = 2.2 \text{ kJ} - (3.0 \text{ mol} \times 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times 25 \text{ K}) = 2.2 \text{ kJ} - 0.62 \text{ kJ} = \underline{1.6 \text{ kJ}}$$

→ Equation 1.5 pts / Answer 1.5 pts (Unit: -1 point)

5. (Total 10 pts)

(a) $\Delta S = C_v \ln(T_2/T_1) = (1 \text{ mol})(1.5)(1.9872 \text{ cal/Kmol})\ln(548\text{K}/298\text{K}) = 1.82 \text{ cal/K} (7.60 \text{ J/K})$
→ Answer 2 pts (Unit, -1 point)

(b) $\Delta S = C_p \ln(T_2/T_1) = (1 \text{ mol})(2.5)(1.9872 \text{ cal/Kmol})\ln(548\text{K}/298\text{K}) = 3.03 \text{ cal/K} (12.7 \text{ J/K})$
→ Answer 2 pts (Unit, -1 point)

For the constant volume process, the gas can't expand, which would result in more disorder and a larger ΔS . Thus, $\Delta S_v < \Delta S_p$.

→ Answer 2 pts (Or if the answer has any sign of the meaning $\Delta S_v < \Delta S_p$)

The isobaric heating results in an increase in V as well as T , where Charles's law gives $V_2 = V_1(T_2/T_1)$. The process can be broken down into a separate isochoric heating stage at V_1 followed by an isothermal expansion at T_2 , giving

$$\Delta S = C_v \ln(T_2/T_1) + nR \ln(V_2/V_1) \quad \text{Up to here: No Any points}$$
$$= C_v \ln(T_2/T_1) + nR \ln(T_2/T_1) = C_p \ln(T_2/T_1) \quad \text{(Up to here, Full 4 pts)}$$

$C_v \ln(T_2/T_1) + nR \ln(V_2/V_1)$ 에 Charles's law $V_2 = V_1(T_2/T_1)$ 를 대입하여 두 번째 식을 쓰고, 끝까지 $C_p \ln(T_2/T_1)$ 를 유도한 경우에만 4점을 주세요. 첫 번째 식만 쓴다면 문제에서 증명하라고 하는 내용을 식으로 정리한 의미 밖에 없습니다.

6. (Total 10 pts)

Mole fractions of Ar and oxygen are:

$$\square (\text{Ar}) = 2.5/(2.5+3.5) = 0.42$$

$$\square (\text{oxygen}) = 3.5/(2.5+3.5) = 0.58$$

$$\Delta S_{\text{mix}} \text{ (5pts)} = -R[n \ln \square (\text{Ar}) + n \ln \square (\text{O})]$$

$$= - (8.314 \text{ J mol}^{-1} \text{K}^{-1}) [(2.5 \text{ mol}) \ln 0.42 + (3.5 \text{ mol}) \ln 0.58] \rightarrow \text{equation: 2 pts}$$

$$= 40 \text{ J K}^{-1}$$

\rightarrow Answer: 3 pts (unit: -1.5 pts)

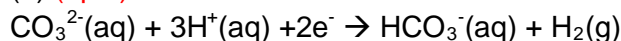
$$\Delta G_{\text{mix}} = -T \Delta S_{\text{mix}}$$

$$\Delta G_{\text{mix}} \text{ (5pts)} = -(298 \text{ K})(40 \text{ J K}^{-1}) = -1.2 \times 10^4 \text{ J}$$

\rightarrow Equation: 2 pts / Answer: 3 pts (unit:-1.5 pts)

7. (Total 10 pts)

(a) (5pts)



$$\Delta G^0 = \Delta_f G^0 (\text{HCO}_3^-) - \Delta_f G^0 (\text{CO}_3^{2-}) = -586.77 \text{ kJ mol}^{-1} - (-527.81 \text{ kJ mol}^{-1}) = \underline{-58.96 \text{ kJ mol}^{-1}}$$

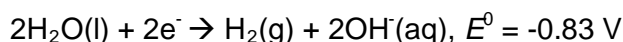
→ 2 pts

$$E^0 = -\Delta G^0 / nF = - (-58.96 \text{ kJ mol}^{-1}) / (2 \times 96485 \text{ J V}^{-1} \text{ mol}^{-1}) = \underline{+0.306 \text{ V}}$$

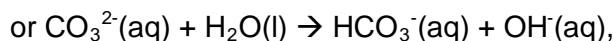
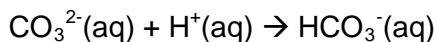
→ Equation: 1.5 pts/ Answer 1.5 (unit -1 point)

(b) (5pts)

Combine the above half-reaction with



which yields;



$$E^0 = \underline{+0.306 \text{ V} - (-0.83 \text{ V})} = \underline{+1.14 \text{ V}}$$

There is an unambiguity in the definition of the cathode in the problem 7(b): in addition to the given half-reaction, $\text{CO}_3^{2-}(\text{aq}) + 3\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{HCO}_3^-(\text{aq}) + \text{H}_2(\text{g})$, a half-reaction, $\text{CO}_3^{2-}(\text{aq}) + 3\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{HCO}_3^-(\text{aq}) + 3\text{OH}^-(\text{aq}) + \text{H}_2(\text{g})$, also can be designed for the cathode. Its emf is calculated to be -0.937 (V) based on the problem 7(a) and the autoionization of water, and other answers could be -0.107 (V) or 0 (V).

Among those who gave the right answer for the problem 7(a), you will additionally be given the full points (5 points) when your answer is -0.1(V) or 0 (V).

→ Equation: 2 pts, answer: 3 pts (Unit -1.5)

(문제 a 의 오답을 대입하여 식이 맞으면, 식에 대한 점수 2 점만 인정.)

(In case the wrong value obtained from (a) is used in this equation, give 2 pts for ONLY right equation.

8. (Total 10 pts)

Using Van't Hoff equation; $\ln(K_2/K_1) = (-\Delta H^\circ/R) \times [(1/T_2)-(1/T_1)] \rightarrow$ **Equation: 2 pts**

$$\begin{aligned}\ln K &= -\Delta G/RT \quad (\Delta G = -nFE^\circ) \\ &= nFE^\circ/RT\end{aligned}$$

$$\ln(K_2/K_1) = \ln K_2 - \ln K_1$$

$$\frac{(nFE^\circ_{\text{cell},T_2}/RT_2) - (nFE^\circ_{\text{cell},T_1}/RT_1)}{RT_2} = (\Delta H^\circ/R) \times [(1/T_1)-(1/T_2)] \rightarrow$$
 Equation: 5 pts

(Where, $T_1 = 25^\circ\text{C} = 298\text{K}$, $T_2 = 80^\circ\text{C} = 353\text{K}$, $E^\circ_{298} = 0.80 - 0.53 = 0.27\text{ V}$; $n = 2\text{ mol}$, $F = 96485\text{ J V}^{-1}\text{ mol}^{-1}$)

$$\therefore \underline{E^\circ_{353} = 0.224\text{V}} \rightarrow$$
 Answer: 3 pts (unit: -1.5 pts)

9. (total 10 pts)

(a) (5 pts)

Horizontally (no additional work to raise the piston)

Work done by the system (w) = distance \times opposing force \times area

$$w = h \times p_{\text{ex}} \times A = 155 \text{ cm} \times 105 \text{ kPa} \times 55.0 \text{ cm}^2 = 895 \text{ Pa m}^3 = \underline{895 \text{ J (or -895 J)}}$$

→ **Equation 2 pts/ answer: 3 pts (unit -1.5 pts)**

(b) (5 pts) Vertically (additional work is required to raise the piston)

$$\text{Additional work} = \underline{mgh = 250 \text{ g} \times 9.81 \text{ m s}^{-2} \times 155 \text{ cm}} = 3.80 \text{ J (or -3.8J)}$$

$$\text{Total work} = \underline{895 \text{ J} + 3.80 \text{ J}} = \underline{899 \text{ J (or -899J)}}$$

→ **Equation 2 pts/ answer: 3 pts (unit -1.5 pts)**

* **Both equations/procedures and answer should be correct to get the point; otherwise, no point is given.**

부연설명

Scoring guides are as follows:

You will get full points ONLY when both answer and equations/procedures are correct (1 point deduction for unit missing).

: 0 pts **even when answer is incorrect and equations/procedures correct.**

: 0 pts **even though answer is correct and equations/procedures incorrect** (In this case, the equation will be checked out whether it is logical or not.).

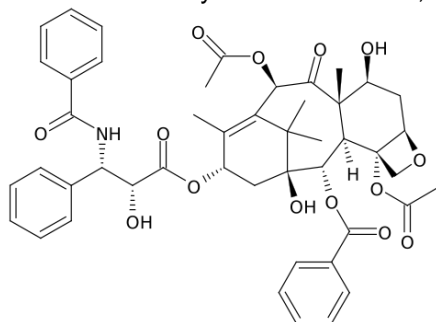
채점기준

식/과정과 답이 다 맞는 경우에만 만점 (단위 없는 경우, -1점 감점)

답이 틀리면 식/과정이 맞더라도 0점 처리

식/과정이 틀리고 답이 맞는 경우에도 0점 (이 경우 식이 논리적인지 확인)

1. (a) (5 pt max.; 1 pt each) Identify the functional groups in the following compound called Paclitaxel or Taxol (Draw the structure in your answer sheet, and indicate your identification in the drawing).

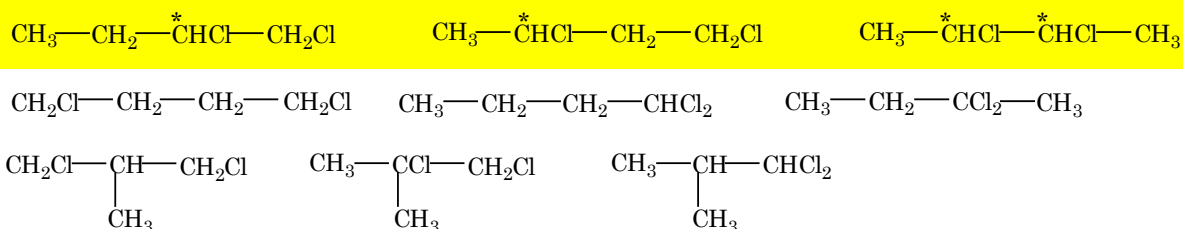


amide, ester, alcohol, ketone, ether

Wrong answer: -1 deduction

(b) (10 pt) Draw all the structural isomers of compounds with the formula $C_4H_8Cl_2$. Indicate which isomers are chiral.

(Answer)



Chiral 3: 1 pt each /9 isomers: 7 pts/8 isomers: 6 pts/7 isomers: 5 pts/6 isomers: 4 pts/5 isomers: 3 pts
 3~4 isomers: 2 pts/1~2 isomers: 1 pt / wrong answer: -1 deduction

The yellow ones are chiral. The asterisk identifies the asymmetric carbon atom.

2. (10 pt) The molar volume of a certain solid is $122.0 \text{ cm}^3 \text{ mol}^{-1}$ at 1.00 atm ($1.013 \times 10^5 \text{ Pa}$) and 483.15 K (its melting temperature). The molar volume of the liquid at this temperature and pressure is $142.6 \text{ cm}^3 \text{ mol}^{-1}$. At $1.26 \times 10^6 \text{ Pa}$, the melting temperature changes to 485.34 K. Calculate the enthalpy and entropy of fusion of the solid.

(Answer)

$$\frac{dp}{dT} = \frac{\Delta S_m}{\Delta V_m}$$

$$\Delta_{\text{fus}} S = \Delta V_m \left(\frac{dp}{dT} \right) \approx \Delta V_m \frac{\Delta p}{\Delta T}$$

assuming $\Delta_{\text{fus}} S$ and ΔV_m independent of temperature.

$$\Delta_{\text{fus}} S = (142.6 \text{ cm}^3 \text{ mol}^{-1} - 122.0 \text{ cm}^3 \text{ mol}^{-1}) \times \frac{(1.26 \times 10^6 \text{ Pa}) - (1.01 \times 10^5 \text{ Pa})}{485.34 \text{ K} - 483.15 \text{ K}}$$

$$= (20.6 \text{ cm}^3 \text{ mol}^{-1}) \times \left(\frac{1 \text{ m}^3}{10^6 \text{ cm}^3} \right) \times (5.29 \times 10^5 \text{ Pa K}^{-1})$$

$$= 10.90 \text{ Pa m}^3 \text{ K}^{-1} \text{ mol}^{-1} = \boxed{10.9 \text{ J K}^{-1} \text{ mol}^{-1}}$$

$$\Delta_{\text{fus}} H = T_i \Delta S = (483.15 \text{ K}) \times (10.90 \text{ J K}^{-1} \text{ mol}^{-1})$$

$$= \boxed{5.27 \text{ kJ mol}^{-1}}$$

3. (10 pt in total) Recently, interest and controversy have surrounded the expansion of liquefied natural gas storage facilities. Joule-Thomson cooling removes heat and impurities, allowing the natural gas to cool to essentially pure $\text{CH}_4(l)$. Some thermodynamical data for CH_4 is given below.

$$\begin{array}{lll} T_f = 90.7 \text{ K} & \Delta H^\circ_{\text{fus}} = 0.29 \text{ kcal/mol} & C_P(s) = 10.2 \text{ cal/K}\cdot\text{mol} \\ T_b = 111.7 \text{ K} & \Delta H^\circ_{\text{vap}} = 1.96 \text{ kcal/mol} & C_P(l) = 12.8 \text{ cal/K}\cdot\text{mol} \\ T_c = 190.5 \text{ K} & & C_P(g) = 8.4 \text{ cal/K}\cdot\text{mol} \\ R = 1.987 \text{ cal/K}\cdot\text{mol} & & \end{array}$$

(a) (2 pt) Determine the highest temperature ($^\circ\text{C}$) at which $\text{CH}_4(l)$ can be stored.

ans. $-82.7 \text{ }^\circ\text{C} = -273.15 + T_c(\text{K})$

(b) (5 pt) Estimate the pressure in atm that is required to store $\text{CH}_4(l)$ at the critical temperature.

$$\ln \frac{P_2}{P_1} = -\frac{\Delta H^\circ_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad \text{or} \quad \frac{d \ln P}{d(1/T)} = -\frac{\Delta H^\circ_{\text{vap}}}{R}$$

(ans. $38.6 \text{ atm} : \ln P_c = (-1960/1.987 \text{ K})(1/190.5 - 1/111.7) = 3.651, P_c = \exp(3.651) = 38.6$)

(c) (3 pt) What is the entropy change from liquid to gas for 1 mol of CH_4 at $P = 1.000 \text{ atm}$ at boiling point?

(ans. $\Delta S = \Delta H/T; 1960/111.7 = 17.5 \text{ cal/K}\cdot\text{mol}$)

4. (10 pt) A flask contains a mixture of compound A and B. Both compounds decompose by first order kinetics. The half-lives are 50.0 min for A and 18.0 min for B. If the concentrations of A and B are equal initially, how long will it take for the concentration of A to be four times that of B?

Both compounds, A and B, decompose by first-order kinetics. Therefore, we can write a first-order rate equation for A and also one for B.

$$\ln \frac{[A]_t}{[A]_0} = -k_A t \qquad \ln \frac{[B]_t}{[B]_0} = -k_B t$$

$$\frac{[A]_t}{[A]_0} = e^{-k_A t} \qquad \frac{[B]_t}{[B]_0} = e^{-k_B t}$$

$$[A]_t = [A]_0 e^{-k_A t} \qquad [B]_t = [B]_0 e^{-k_B t}$$

We can calculate each of the rate constants, k_A and k_B , from their respective half-lives.

$$k_A = \frac{0.693}{50.0 \text{ min}} = 0.0139 \text{ min}^{-1} \qquad k_B = \frac{0.693}{18.0 \text{ min}} = 0.0385 \text{ min}^{-1}$$

The initial concentration of A and B are equal. $[A]_0 = [B]_0$. Therefore, from the first-order rate equations, we can write:

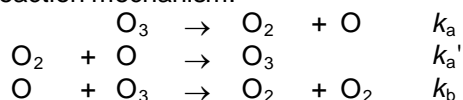
$$\frac{[A]_t}{[B]_t} = 4 = \frac{[A]_0 e^{-k_A t}}{[B]_0 e^{-k_B t}} = \frac{e^{-k_A t}}{e^{-k_B t}} = e^{(k_B - k_A)t} = e^{(0.0385 - 0.0139)t}$$

$$4 = e^{0.0246t}$$

$$\ln 4 = 0.0246t$$

$$t = 56.4 \text{ min}$$

5. (10 pt) Derive the rate law for the decomposition of O_3 , $2O_3(g) \rightarrow 3O_2(g)$, on the basis of the following reaction mechanism:



(Answer)

The intermediate is O; by using the steady-state approximation the net rate of change of its concentration is 0.

$$\frac{d[O]}{dt} = k_a[O_3] - k_a'[O_2][O] - k_b[O][O_3] \approx 0 \rightarrow [O] = \frac{k_a[O_3]}{k_a'[O_2] + k_b[O_3]}$$

The net rate of change of concentration of O_3 is

$$\frac{d[O_3]}{dt} = -k_a[O_3] + k_a'[O_2][O] - k_b[O][O_3]$$

and replacing the concentration of the intermediate by using the equation above gives

$$\begin{aligned} \frac{d[O_3]}{dt} &= -k_a[O_3] + (k_a'[O_2] - k_b[O_3]) \frac{k_a[O_3]}{k_a'[O_2] + k_b[O_3]} \\ &= \frac{-k_a k_a'[O_3][O_2] - k_a k_b[O_3]^2 + k_a k_a'[O_3][O_2] - k_a k_b[O_3]^2}{k_a'[O_2] + k_b[O_3]} = \frac{-2k_a k_b[O_3]^2}{k_a'[O_2] + k_b[O_3]} \end{aligned}$$

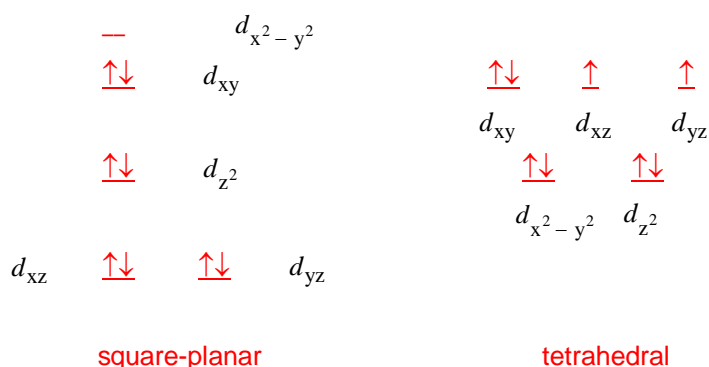
Therefore the rate law is

$$Rate = -\frac{1}{2} \frac{d[O_3]}{dt} = \frac{k_a k_b [O_3]^2}{k_a' [O_2] + k_b [O_3]}$$

6. (4 pt each) Choose the word(s) that describe(s) the left one correctly.

- | | |
|--------------------------|---|
| (a) $[Co(NH_3)_6]^{3+}$ | (paramagnetic, diamagnetic) |
| (b) $[Pt(NH_3)_4]^{2+}$ | (planar , tetrahedral) |
| (c) CN^- | (weak field ligand, strong field ligand) |
| (d) Strong field ligands | (π acceptors , π donors) |
| (e) $[Co(NH_3)_4Cl_2]^-$ | (achiral , chiral) |

7. (5 pt) The atomic number of Ni is 28. The Ni^{2+} cation can form a complex ion with four CN^- anions. The resultant $[Ni(CN)_4]^{2-}$ is found to have a diamagnetic property. Based on the crystal field theory, predict the geometry of $[Ni(CN)_4]^{2-}$.



The square-planar complex is diamagnetic, because there is no unpaired electron. The tetrahedral complex is paramagnetic, because there are 2 unpaired electrons. Therefore, $[Ni(CN)_4]^{2-}$ has a square-planar geometry.

8. (4 pt each) Choose the right word(s).

(a) The absorption wavelength of $[\text{Cr}(\text{CN})_6]^{3-}$ is (**shorter**, longer) than that of $[\text{Cr}(\text{NH}_3)_6]^{3+}$.

(b) Both $[\text{Pt}(\text{en})_3]^{4+}$ and $[\text{CoEDTA}]^-$ are chiral. (**true**, false)

(c) **Nylon-66** is formed in the (**condensation**, addition) reaction.

(d) The vapor pressure of A as a solvent is (more, **less**) than that of A(l) by a factor of its (concentration, **mole fraction**, pressure).

(e) The following compounds are arranged in order of increasing T_b : CH_3F , CH_3Cl , CH_3Br , CH_3I . The electronegativity difference between the C atom and the halogen might lead one to expect that (**dipole-dipole**, hydrogen bonding, charge-induced dipole, London dispersion) forces would have a large effect on the T_b ordering. The actual order, however, suggests that (dipole-dipole, hydrogen bonding, charge-induced dipole, **London dispersion**) forces must have the far greater influence over the observed T_b trend.