

## EXAM 2

1)

a.

$$\Delta G^\circ_{\text{rxn}} = (-133 \text{ kJ mol}^{-1}) + (-394 \text{ kJ mol}^{-1}) - (-463 \text{ kJ mol}^{-1})$$

$$= -64 \text{ kJ mol}^{-1}$$

$\Delta G^\circ_{\text{rxn}} < 0 \rightarrow$  This reaction is spontaneous under standard state conditions

b.

$$\Delta H^\circ_{\text{rxn}} = (-166 \text{ kJ mol}^{-1}) + (-394 \text{ kJ mol}^{-1}) - (-584 \text{ kJ mol}^{-1})$$

$$= 24 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ_{\text{rxn}} = \frac{\Delta H^\circ_{\text{rxn}} - \Delta G^\circ_{\text{rxn}}}{T} = \frac{24 \text{ kJ mol}^{-1} - (-64 \text{ kJ mol}^{-1})}{298 \text{ K}}$$

$$= 0.295 \text{ kJ mol}^{-1} \text{ K}^{-1}$$

$$\Delta G^\circ(80 \text{ K}) = 24 \text{ kJ mol}^{-1} - (80 \text{ K})(0.295 \text{ kJ mol}^{-1} \text{ K}^{-1})$$

$$= 0.40 \text{ kJ mol}^{-1}$$

$$K = e^{-\Delta G^\circ(80 \text{ K}) / RT} = e^{-(0.40 \times 10^3 \text{ J mol}^{-1}) / (8.314 \text{ J mol}^{-1} \text{ K}^{-1})(80 \text{ K})}$$

$$= 0.548$$

c.

At low temp, the reaction favors the reactants

2)

a.

$$dA = -SdT - PdV = \left(\frac{\partial A}{\partial T}\right)_V dT + \left(\frac{\partial A}{\partial V}\right)_T dV$$

$$\rightarrow \left(\frac{\partial A}{\partial T}\right)_V = -S \quad \text{and} \quad \left(\frac{\partial A}{\partial V}\right)_T = -P$$

$$\left. \begin{aligned} \frac{\partial}{\partial V} \left(\frac{\partial A}{\partial T}\right)_V &= -\left(\frac{\partial S}{\partial V}\right)_T \\ \frac{\partial}{\partial T} \left(\frac{\partial A}{\partial V}\right)_T &= -\left(\frac{\partial P}{\partial T}\right)_V \\ \frac{\partial}{\partial V} \left(\frac{\partial A}{\partial T}\right)_V &= \frac{\partial}{\partial T} \left(\frac{\partial A}{\partial V}\right)_T \end{aligned} \right\} \rightarrow \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V = \frac{P}{nK}$$

$$\rightarrow \left(\frac{\partial S_m}{\partial V}\right)_T = \frac{P}{nK}$$



b.

Increasing volume  $\rightarrow$  increasing molar entropy

c.

$$dG = -SdT + VdP = -\left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP$$

$$\rightarrow \left(\frac{\partial G}{\partial P}\right)_T = V$$

$$\left\{ \begin{aligned} \frac{\partial}{\partial n_i} \left( \frac{\partial G}{\partial P} \right)_T &= \left( \frac{\partial V}{\partial n_i} \right)_{T, P, n_{j \neq i}} \\ \frac{\partial}{\partial n_i} \left( \frac{\partial G}{\partial P} \right)_T &= \frac{\partial}{\partial P} \left( \frac{\partial G}{\partial n_i} \right)_{P, T, n_{j \neq i}} = \left( \frac{\partial \mu_i}{\partial P} \right)_{T, n_{j \neq i}} \end{aligned} \right.$$

$$\rightarrow \left( \frac{\partial V}{\partial n_i} \right)_{T, P, n_{j \neq i}} = \left( \frac{\partial \mu_i}{\partial P} \right)_{T, n_{j \neq i}}$$

d.

$$\begin{aligned} \left( \frac{\partial \mu_{\text{COCl}_2}}{\partial P} \right)_{T, n_{\text{CO}}, n_{\text{Cl}_2}} &= \left( \frac{\partial V}{\partial n_{\text{COCl}_2}} \right)_{T, P, n_{\text{CO}}, n_{\text{Cl}_2}} \\ &= \left( \frac{\partial (nRT/P)}{\partial n_{\text{COCl}_2}} \right)_{T, P, n_{\text{CO}}, n_{\text{Cl}_2}} \\ &= \frac{RT}{P} \frac{\partial (n_{\text{COCl}_2} + n_{\text{CO}} + n_{\text{Cl}_2})}{\partial n_{\text{COCl}_2}} \\ &= \frac{RT}{P} \left( \frac{\partial n_{\text{COCl}_2}}{\partial n_{\text{COCl}_2}} + \frac{\partial n_{\text{CO}}}{\partial n_{\text{COCl}_2}} + \frac{\partial n_{\text{Cl}_2}}{\partial n_{\text{COCl}_2}} \right) \\ &= \frac{RT}{P} (1 - 1 - 1) = -\frac{RT}{P} \end{aligned}$$

$$\rightarrow \left( \frac{\partial \mu_{\text{COCl}_2}}{\partial P} \right)_{T, n_{\text{CO}}, n_{\text{Cl}_2}} = -\frac{RT}{P}$$

Increasing pressure  $\rightarrow$  decreasing chemical potential

e.

$$\left( \frac{\partial \mu_{\text{COCl}_2}}{\partial P} \right)_{T, n_{\text{CO}}, n_{\text{Cl}_2}} = -\frac{RT}{P}$$



$$\rightarrow d\mu_{\text{CO}_2} = -\frac{RT}{P} dP$$

$$\int d\mu_{\text{CO}_2} = \int -\frac{RT}{P} dP$$

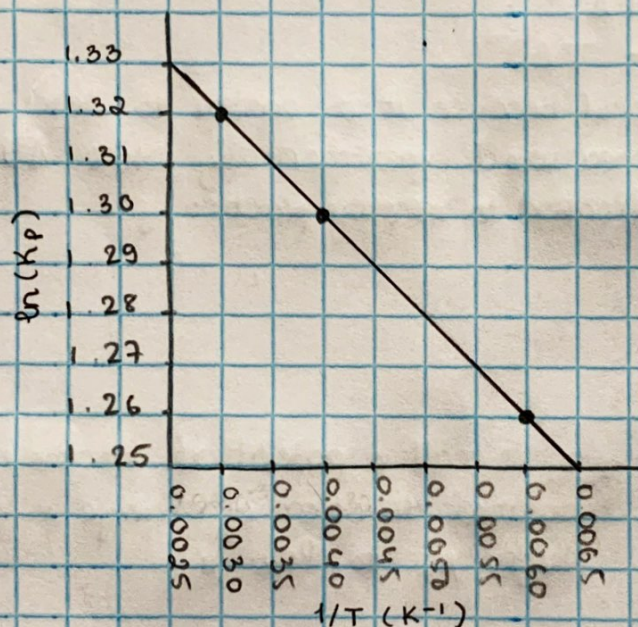
$$\mu_{\text{CO}_2} - \mu_{\text{CO}_2}^{\circ} = -RT \ln \frac{P}{P^{\circ}}$$

$$\mu_{\text{CO}_2} = \mu_{\text{CO}_2}^{\circ} - RT \ln \frac{P}{P^{\circ}}$$

3.

a.

$1/T$	$\ln K_p$
$6 \times 10^{-3}$	1.26
$4 \times 10^{-3}$	1.30
$3 \times 10^{-3}$	1.32



b.

$$\frac{\Delta H^{\circ}}{R} = \frac{1.32 - 1.30}{0.0030 \text{ K}^{-1} - 0.004 \text{ K}^{-1}} = -20 \text{ K}$$

$$\rightarrow \Delta H^{\circ} = -(-20 \text{ K}) \times (8.314 \text{ J mol}^{-1} \text{ K}^{-1}) = 166.28 \text{ J mol}^{-1}$$

$$1.26 = -20 (6 \times 10^{-3}) + \frac{\Delta S^{\circ}}{R} \rightarrow \frac{\Delta S^{\circ}}{R} = 1.38$$

$$\rightarrow \Delta S^{\circ} = 1.38 \times (8.314 \text{ J mol}^{-1} \text{ K}^{-1}) = 11.47 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\begin{aligned} \Delta G^{\circ} &= 166.28 \text{ J mol}^{-1} - (298 \text{ K})(11.47 \text{ J mol}^{-1} \text{ K}^{-1}) \\ &= -3251.8 \text{ J mol}^{-1} \end{aligned}$$

c.

Reaction is entropically driven because the reaction is spontaneous as  $\Delta S^{\circ} > 0$ ,  $\Delta H^{\circ} < 0$



4.

Second Law of Thermodynamics: The total entropy of an isolated system can never decrease over time, and is constant only if all processes are reversible.

5.

- Third law of Thermodynamics: The entropy of a pure, perfectly crystalline substance (element or compound) is 0 at 0K.
- Entropy has absolute zero value.

6.

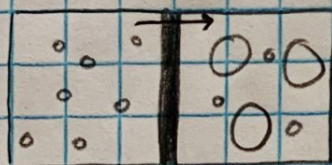
- Because of second law of thermodynamics, heat cannot be converted to work completely.

7.

- Gibbs Energy  $\Delta G = \Delta H^\circ - T\Delta S^\circ$
- Helmholtz Energy  $\Delta A = \Delta U - T\Delta S^\circ$
- Gibbs free energy is more useful because it is easier to determine from  $\Delta H^\circ$  and  $\Delta S$  that are both measured experimentally while  $\Delta U$  for Helmholtz energy is more complicated to measure practically.

8.

$$\mu_i = \left( \frac{\partial G}{\partial n} \right)_{P, T, n_j \neq i}$$



○ He atom  
● H atom

- $\mu_i$  is called a potential because the natural direction of change is from high  $\mu_i$  to low  $\mu_i$ .

Pd membrane  
allows only  $H_2$   
to go through

9.

Mixing of different types of molecules in an ideal gas is spontaneous.

$$\Delta G_{\text{mixing}}^\circ = nRT \sum_i x_i \ln x_i$$

$$0 < x_i < 1 \rightarrow \ln x_i < 0 \quad \left. \vphantom{\sum_i x_i \ln x_i} \right\} \rightarrow \Delta G_{\text{mixing}}^\circ < 0$$



10.

$$K_p = e^{-\Delta G^\circ / RT}$$

$$\Delta G^\circ > 0 \rightarrow -\frac{\Delta G^\circ}{RT} < 0 \rightarrow e^{-\Delta G^\circ / RT} < 1 \rightarrow K_p < 1$$

→ More reactants.

### Extra credit

• van't Hoff equation :  $\ln K_e = \left( -\frac{\Delta H^\circ}{R} \right) \frac{1}{T} + \frac{\Delta S^\circ}{R}$

• Shows the temperature dependence of equilibrium constant.

$$-RT \ln K = \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$$

$$\rightarrow \ln K = -\frac{\Delta H^\circ}{R} \left( \frac{1}{T} \right) + \frac{\Delta S^\circ}{R}$$