

Exam #2: 4-2-2020: **Please show all work for credit**, Don't Panic

Name: \_\_\_\_\_

**Important:** This exam must be turned in handwritten. It can be on lined paper.

**It must be turned in as a single PDF. Image files for each page will not be accepted.**

You can download Adobe Scan on your phone to make the PDF.

<https://acrobat.adobe.com/us/en/mobile/scanner-app.html>

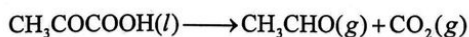
Who did you work with?

- a. Samantha Jacques
- b. Alicia Lumia
- c. Kovi Ramotar
- d.

Who else did you ask for help?

Name: Kavirish Ramotar

1. The decarboxylation of pyruvic acid occurs via the following reaction:



Given the following thermodynamic data  $\rightarrow$   $\Delta H_{\text{rxn}}^\circ = (-166 \text{ kJ mol}^{-1} + -394 \text{ kJ mol}^{-1}) - (-584 \text{ kJ mol}^{-1})$   
 $\Delta H_{\text{rxn}}^\circ = 24 \text{ kJ mol}^{-1}$

$$\Delta_f H(25 \text{ C})_{\text{CH}_3\text{COCO}(\text{OH})} = -584 \text{ kJ mol}^{-1} \quad \Delta_f G(25 \text{ C})_{\text{CH}_3\text{COCO}(\text{OH})} = -463 \text{ kJ mol}^{-1}$$

$$\Delta_f H(25 \text{ C})_{\text{CH}_3\text{CHO}} = -166 \text{ kJ mol}^{-1} \quad \Delta_f G(25 \text{ C})_{\text{CH}_3\text{CHO}} = -133 \text{ kJ mol}^{-1}$$

$$\Delta_f H(25 \text{ C})_{\text{CO}_2} = -394 \text{ kJ mol}^{-1} \quad \Delta_f G(25 \text{ C})_{\text{CO}_2} = -394 \text{ kJ mol}^{-1}$$

a. Calculate  $\Delta G_{\text{rxn}}^\circ$ . Is this reaction spontaneous under standard state conditions? Justify your answer.

$$\Delta G_{\text{rxn}}^\circ = (\Delta_f G^\circ(\text{CH}_3\text{CHO}, \text{g}) + \Delta_f G^\circ(\text{CO}_2, \text{g})) - \Delta_f G^\circ(\text{CH}_3\text{COCO}(\text{OH}), \text{l})$$

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

$$\Delta G_{\text{rxn}}^\circ = -64 \text{ kJ mol}^{-1}$$

This reaction is spontaneous under standard state conditions because  $\Delta G_{\text{rxn}}^\circ$  is a negative value.

b. Calculate the equilibrium constant,  $K_p$ , for this reaction at 80.0 K.

$$\ln K_p(80 \text{ K}) = \frac{\Delta G^\circ}{RT} - \frac{\Delta H^\circ}{R} \left( \frac{1}{T_f} - \frac{1}{298 \text{ K}} \right)$$

$$\ln K_p(80 \text{ K}) = \frac{-(-64 \times 10^3 \text{ J mol}^{-1})}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})} - \frac{24 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \left( \frac{1}{80 \text{ K}} - \frac{1}{298 \text{ K}} \right)$$

$$\ln K_p(80 \text{ K}) = -0.565$$

$$K_p = 0.568 \text{ at } 80.0 \text{ K}$$

c. At the lower temperature, does the reaction favor the reactants or the products?

At the lower temperature, the reaction favors the reactants because  $K_p$  is very small and the reaction is less spontaneous.

$$\begin{aligned}
 2A. \quad \left(\frac{\partial S}{\partial V}\right)_T &= \left(\frac{\partial P}{\partial T}\right)_V \\
 \beta &= \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P \quad K = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T \\
 \beta V &= \left(\frac{1}{K_V}\right) = -\left(\frac{\partial P}{\partial T}\right)_V \\
 \left(\frac{\partial P}{\partial T}\right)_V &= \frac{\beta}{K} \\
 \left(\frac{\partial S_m}{\partial V}\right)_T &= \frac{\beta}{nK}
 \end{aligned}$$

B.  $\beta$ ,  $K$ , and  $n$  are positive  
therefore making the whole term positive which means entropy increases

$$\begin{aligned}
 C. \quad \left(\frac{\partial U_i}{\partial P}\right)_{T, n_i \neq 1} &= \left(\frac{\partial V}{\partial n_i}\right)_{T, P, n_j \neq 1} \\
 V &= \frac{\partial(n b_i)}{\partial P} \Rightarrow \frac{\partial V}{\partial n_i} = \frac{\partial^2(n b_i)}{\partial n_i \partial P}
 \end{aligned}$$

$$\mu_i = \frac{\partial(n b_i)}{\partial n_i} \Rightarrow \frac{\partial \mu_i}{\partial P} = \frac{\partial^2(n b_i)}{\partial n_i \partial P}$$

$$\frac{\partial V}{\partial n_i} = \frac{\partial \mu_i}{\partial P}$$

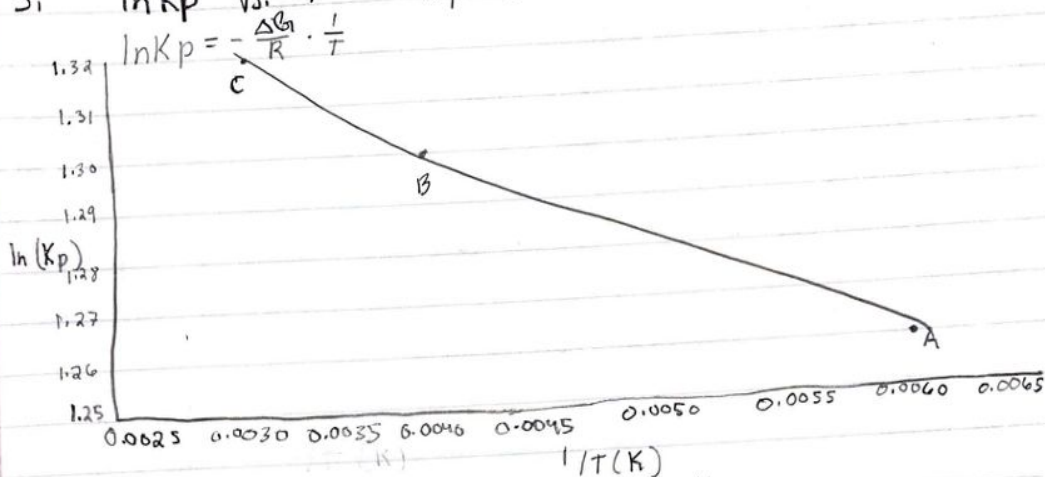
$$\begin{aligned}
 D. \quad \left(\frac{\partial U_{COCl_2}}{\partial P}\right)_{T, n_{CO}, n_{Cl_2}} &= \left(\frac{\partial V}{\partial n_{COCl_2}}\right)_{T, P, n_{CO}, n_{Cl_2}} \\
 \left(\frac{\partial U_{COCl_2}}{\partial P}\right)_{T, n_{CO}, n_{Cl_2}} &= \left(\frac{\partial V}{\partial n_{COCl_2}}\right)_{T, P, n_{CO}, n_{Cl_2}}
 \end{aligned}$$

Chemical potential increases when the pressure increases. When the pressure is increased the equilibrium moves to the side with the fewest moles.

There will be an increase of formation as the pressure increases

$$\begin{aligned}
 E. \quad \left(\frac{\partial U_{COCl_2}}{\partial P}\right)_{T, n_{CO}, n_{Cl_2}} &= \left(\frac{\partial V}{\partial n_{COCl_2}}\right)_{T, P, n_{CO}, n_{Cl_2}} \\
 \int_{P_0}^P \partial \mu_i &= (\mu_i - \mu_{i,0}) \\
 \int_{P_0}^P \frac{\partial V}{\partial n_i} \partial P &= \frac{\partial V}{\partial n_i} (P - P_0) \\
 \mu_i - \mu_{i,0} &= \frac{\partial V}{\partial n_i} (P - P_0)
 \end{aligned}$$

3.  $\ln K_p$  vs.  $\frac{1}{T}$   $K_p = e^{-\Delta G^\circ/RT}$



	T(K)	K <sub>p</sub>		1/T(K)	y
A.	167	3.53	→ A.	0.0059	1.26
B.	250	3.67	→ B.	0.004	1.30
C.	333	3.74	→ C.	0.003	1.32

b. Slope =  $\frac{y_2 - y_1}{x_2 - x_1} = 20.69$

$-\frac{\Delta G^\circ}{R} = \text{slope}$

$\Delta G^\circ = 20.69 \times 8.314 \text{ J/mol K}$

$\Delta G^\circ = 172.02 \text{ J/mol}$

$\Delta G^\circ$  is positive therefore the reaction is not spontaneous

c. The reaction is enthalpically because

$$\frac{d \ln K_p}{dT} = \frac{\Delta H_r}{RT^2}$$



4) The second law of thermodynamics is:

- There is a quantity (entropy) that can never decrease over time in an isolated system.
- $\Delta S \geq 0$  for any process in an isolated system.
- $\Delta S < 0$  for the opposite / nonspontaneous direction of change
- $\Delta S = 0$  only for a reversible process.
- $\Delta S_{\text{universe}} \geq 0$
- Do not need to know about molecules.
- A cyclic process cannot convert heat to work with 100% efficiency.

5) The third law of thermodynamics is:

- The entropy of a pure, perfectly crystalline substance (element or compound) is zero at zero Kelvin.

- $S = k \ln(w)$
- $\Delta X \Delta P \geq \frac{\hbar}{2}$

- $\Delta X \Delta P \neq 0$

6) We cannot build a perpetual motion machine because:

- The 1<sup>st</sup> Law

- More energy cannot be created

- The perpetual motion machine would need more energy to keep moving. This is impossible!

7) Gibbs free energy is usually more useful to chemists than Helmholtz energy because: Gibbs energy:

$$d(H-TS) \leq \delta w_{\text{expansion}} - SdT + VdP$$

$$dG \leq \delta w_{\text{nonexpansion}} - SdT + VdP, G \equiv H-TS$$

• At constant volume & pressure:

$$\Delta G \leq 0, \Delta G_r < 0$$

• Negative Gibbs energy if process is spontaneous

$$\Delta G_r = \Delta H_r - T\Delta S_r$$

8) Chemical Potential:



$dn_i \rightarrow$

$$\Delta T, \Delta P = 0$$

$$\mu_i^I > \mu_i^{II}$$

Species 'i' in one of two regions system is set up so that:  $\mu_i^I > \mu_i^{II}$

$$dG = -\underbrace{\mu_i^I}_{\text{region I}} dn_i + \underbrace{\mu_i^{II}}_{\text{gains molecules}} dn_i = (\underbrace{\mu_i^{II} - \mu_i^I}_{\text{always negative}}) dn_i < 0$$

region I  
loses molecules

gains  
molecules

always  
negative

• Natural direction of change dictated by chemical potential:



• Gives standard free energy of reaction.

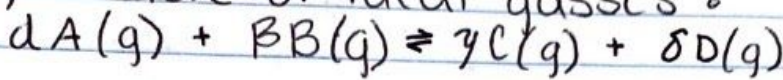
• Natural direction of change dictated by gravitational potential.

• Always high  $\rightarrow$  low





q) Mixture of ideal gasses :



$$\Delta G_R = \sum_i \nu_i \Delta G_{f,i} = \gamma \mu_C^0 + \gamma RT \ln \frac{P_C}{P^0} + \delta \mu_D^0 + \delta RT \ln \frac{P_D}{P^0} - \alpha \mu_A^0 - \alpha RT \ln \frac{P_A}{P^0} - \beta \mu_B^0 - \beta RT \ln \frac{P_B}{P^0}$$

Chemical Potentials give standard free energy of reaction  
 $\Delta G_R^0 = \gamma \mu_C^0(T) + \delta \mu_D^0(T) - \alpha \mu_A^0(T) - \beta \mu_B^0(T) = \sum_i \nu_i \Delta G_{f,i}^0$

$$\Delta G_R^0 + RT \ln \frac{\left(\frac{P_C}{P^0}\right)^\gamma \left(\frac{P_D}{P^0}\right)^\delta}{\left(\frac{P_A}{P^0}\right)^\alpha \left(\frac{P_B}{P^0}\right)^\beta} \quad Q_P = \frac{\left(\frac{P_C}{P^0}\right)^\gamma \left(\frac{P_D}{P^0}\right)^\delta}{\left(\frac{P_A}{P^0}\right)^\alpha \left(\frac{P_B}{P^0}\right)^\beta}$$

$$\Delta G_R = \Delta G_R^0 + RT \ln Q_P$$

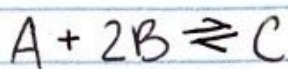
$$0 = \Delta G_R^0 + RT \ln K_P, \quad K_P = e^{\Delta G_R^0 / RT}$$

$$10) \quad \Delta G^{\circ}_{\text{rxn}} = -RT \ln K_{\text{eq}} \\ \Delta G^{\circ}_{\text{rxn}} > 0$$

$$\ln K_{\text{eq}} < 0$$

$$K_{\text{eq}} = \frac{[\text{products}]}{[\text{reactants}]} < 1$$

$$[\text{product}] < [\text{reactant}]$$



$$\Delta G^{\circ} > 0$$

$$-RT \ln K_{\text{eq}} > 0$$

$$K_{\text{eq}} < 1$$

$$K_{\text{eq}} = \frac{[C]}{[A][B]^2} < 1$$

$$[A][B]^2 > [C]$$

Therefore reactants are favored over products  
if  $\Delta G^{\circ}_{\text{rxn}} > 0$ .

- Extra Credit:

Favorite Equation: Internal Energy

$$\Delta U = U_f - U_i$$

• It gives the sum of the energies of all the particles in a system, with respect to the internal coordinate system.