

# Exam #2

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Who did you work with?

a) Angela Tran

b) Phuong Le

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Who else did you ask for help?

No one.

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

$$\text{CH}_3\text{COCOOH}_{(l)} \rightarrow \text{CH}_3\text{CHO}_{(g)} + \text{CO}_{2(g)}$$

Given the thermodynamic data

$$\Delta_f H(25^\circ\text{C})_{\text{CH}_3\text{COCOOH}} = -584 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta_f G(25^\circ\text{C})_{\text{CH}_3\text{COCOOH}} = -463 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta_f H(25^\circ\text{C})_{\text{CH}_3\text{CHO}} = -166 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta_f G(25^\circ\text{C})_{\text{CH}_3\text{CHO}} = -133 \frac{\text{kJ}}{\text{mol}}$$

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

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

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

$$\Delta G_{\text{rxn}}^\circ = [(-394 \frac{\text{kJ}}{\text{mol}}) + (-133 \frac{\text{kJ}}{\text{mol}})] - [-463 \frac{\text{kJ}}{\text{mol}}] = -527 \frac{\text{kJ}}{\text{mol}} + 463 \frac{\text{kJ}}{\text{mol}} = -64 \frac{\text{kJ}}{\text{mol}}$$

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

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

$$K_p(298\text{K}) = e^{-\frac{\Delta G}{RT}} = e^{-\frac{64000 \frac{\text{J}}{\text{mol}}}{8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}} \cdot 298\text{K}}} = 1.65 \cdot 10^{11}$$

$$\Delta H_{\text{rxn}}^\circ = [(-394) + (-166)] - [-584] \frac{\text{kJ}}{\text{mol}} = 24 \frac{\text{kJ}}{\text{mol}} = 24000 \frac{\text{J}}{\text{mol}}$$

$$\ln(K_p(80\text{K})) = \ln K_p(298\text{K}) - \frac{\Delta H_{\text{rxn}}^\circ}{R} \left( \frac{1}{80\text{K}} - \frac{1}{298\text{K}} \right)$$

$$\rightarrow K_p(80\text{K}) = e^{11(1.65 \cdot 10^{11}) - \frac{24000 \frac{\text{J}}{\text{mol}}}{8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}} \left( \frac{1}{80\text{K}} - \frac{1}{298\text{K}} \right)}} = 0.56$$

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

At the lower temperature the reaction favors the reactants, as  $K_p < 1$ .

2. For a pure substance

a) Derive the following expression:  $\left(\frac{\partial S_m}{\partial V}\right)_T = \frac{\beta}{nK}$

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV = \frac{1}{T} dU - \frac{V}{T} dP = \frac{1}{T} dU + \frac{P}{T} dV + \frac{V}{T} dP - \frac{V}{T} dP$$

$$dS = \frac{C_V}{T} dT + \frac{1}{T} \left( T \left(\frac{\partial P}{\partial T}\right)_V dV \right) - \frac{P}{T} dV + \frac{P}{T} dV$$

$$dS = \frac{C_V}{T} dT + \frac{\beta}{K} dV$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{\beta}{K} \rightarrow \text{to get molar } S_m, \text{ need to divide by } n \rightarrow \left(\frac{\partial S_m}{\partial V}\right) = \frac{\beta}{nK}$$

b) How does the molar entropy change with increasing volume?

With increasing volume the molar entropy also increases.  $dS_m \propto dV$

For a mixture of substances,  $n_1, n_2, n_3, \dots$

c) Show that the pressure dependence of the chemical potential is related to the volume as follows  $\left(\frac{\partial \mu_i}{\partial P}\right)_{T, n_j \neq i} = \left(\frac{\partial V}{\partial n_i}\right)_{T, P, n_j \neq i}$

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

$$\rightarrow \left(\frac{\partial G}{\partial T}\right)_P = -S \quad \left(\frac{\partial G}{\partial P}\right)_T = V$$

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

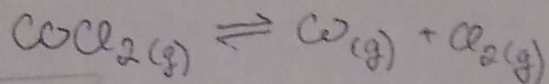
$$\frac{\partial}{\partial n_i} \left(\frac{\partial G}{\partial P}\right) = \frac{\partial}{\partial P} \left(\frac{\partial G}{\partial n_i}\right) = \left(\frac{\partial \mu_i}{\partial P}\right)_{T, n_j \neq i}$$

equal to each other  
 $\left(\frac{\partial}{\partial n_i} \left(\frac{\partial G}{\partial P}\right)\right)$  for both

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



d) Pure phosphine is allowed to decompose according to the following reaction



Assuming ideal gas behaviour, & using the Maxwell relationship above, derive an expression for  $\left(\frac{\partial \mu_{\text{COCl}_2}}{\partial P}\right)_{T, n_{\text{CO}}, n_{\text{Cl}_2}}$

How does the chemical potential change with increasing pressure?

Hint:  $n = n_{\text{COCl}_2} + n_{\text{CO}} + n_{\text{Cl}_2}$   $d\mu_{\text{COCl}_2} = -dn_{\text{CO}}$   $dn_{\text{COCl}_2} = -dn_{\text{Cl}_2}$

$$\left(\frac{\partial \mu_{\text{COCl}_2}}{\partial P}\right)_{T, n_{\text{CO}}, n_{\text{Cl}_2}} = \left(\frac{\partial V}{\partial n_{\text{COCl}_2}}\right)_{T, P, n_{\text{CO}}, n_{\text{Cl}_2}} \quad \text{ideal gas}$$

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

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

With increasing pressure, the chemical potential decreases ( $d\mu \propto \frac{1}{dP}$ )

e) Use your result in part d to derive an expression for  $\mu_{\text{COCl}_2}(P)$  with respect to some reference pressure,  $P^0$ .

$$\left(\frac{\partial \mu_{\text{COCl}_2}}{\partial P}\right) = -\frac{RT}{P}$$

$$d\mu_{\text{COCl}_2} = -\frac{RT}{P} dP \quad / \int$$

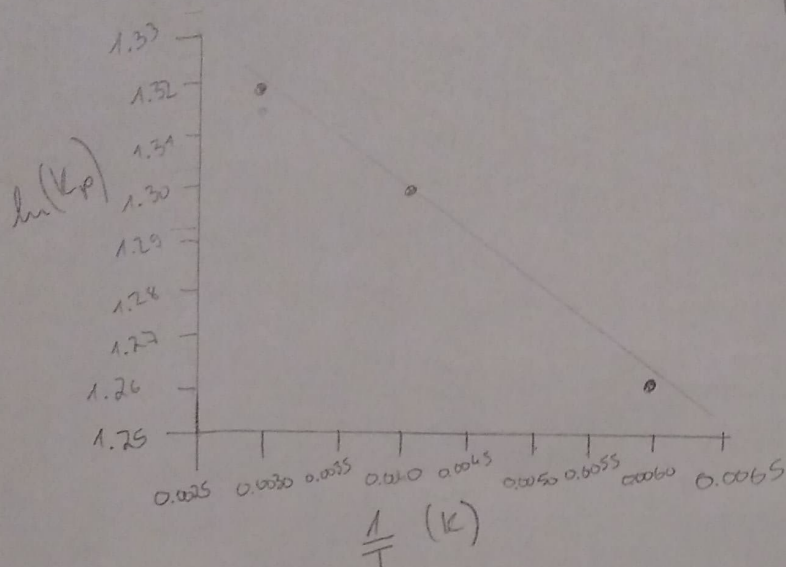
$$\boxed{\mu_{\text{COCl}_2} - \mu_{\text{COCl}_2}^0 = -RT \ln \frac{P}{P^0}}$$

3. The following thermodynamic data was measured for a chemical reaction.

$T(K)$	$K_p$	$\frac{1}{T}(K)$	$\ln K_p$
167	3.53	0.0059882	1.261
250	3.67	0.004	1.300
333	3.74	0.003003	1.319

a) Plot the data on the following plot.

(plot not to scale)



b) Calculate  $\Delta G_r^\circ$  for this reaction. Is this reaction spontaneous? Justify your answer.

$$\text{line: } \ln K_p = -\frac{\Delta H^\circ}{R} \left( \frac{1}{T} \right) + \frac{\Delta S^\circ}{R}$$

$$\text{slope} = \frac{\text{rise}}{\text{run}} = \frac{1.319 - 1.261}{0.003003 - 0.005988} = -19.43 = -\frac{\Delta H^\circ}{R}$$

$$\Delta H = 161.5 \frac{\text{J}}{\text{mol}}$$

$$1.300 = -19.43(0.004) + \frac{\Delta S^\circ}{R}$$

$$\frac{\Delta S^\circ}{R} = 1.378$$

$$\Delta S^\circ = 11.45 \frac{\text{J}}{\text{mol K}}$$

$$\rightarrow \Delta G_R^\circ = \Delta H_R^\circ - T \Delta S_R^\circ$$

$$= 161.5 \frac{\text{J}}{\text{mol}} - 298\text{K} \cdot 11.45 \frac{\text{J}}{\text{mol K}}$$

$$\Delta G_R^\circ = -3250.6 \frac{\text{J}}{\text{mol}}$$

The reaction is spontaneous because  $\Delta G_R^\circ < 0$

c) Is this reaction enthalpically or entropically driven? Justify your answer.

Since  $\Delta H_r^\circ$  is positive, the reaction depends on the  $\Delta S_r^\circ$  to be more positive to make  $\Delta G_r^\circ$  negative. Therefore, the reaction is entropically driven for  $\Delta G_r^\circ$  to be negative & the reaction to be spontaneous.



Short answers:

4. What is the 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. For any irreversible process in an isolated system, there is a unique direction of spontaneous change.

5. What is the third law of thermodynamics? Explain how this makes entropy different than energy or enthalpy.

The entropy of a pure, perfectly crystalline substance is zero at 0 K. Entropy can have an absolute value, while energy & enthalpy only have relative values.

6. Why can't we build a perpetual motion machine?

We can't build a perpetual motion machine because the work output by any machine is always smaller than the heat absorbed (from Second law of thermodynamics).

$$E = \frac{-w_{\text{cycle}}}{q_{\text{absorbed}}} < 1$$

7. Why is Gibbs's free energy usually more useful to chemists than Helmholtz energy?

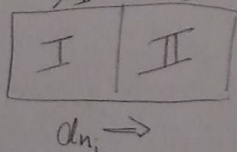
Gibbs's free energy is  $\Delta G = \Delta(H - TS)$

Helmholtz energy is  $\Delta A = \Delta(U - TS)$

Gibbs's free energy is usually more useful as it is easier to measure  $H$ , through heat, than  $U$ , the internal energy.

8. Give the mathematical definition of chemical potential. Explain why it is called a potential. Include at least one drawing.

$$\frac{\partial G}{\partial n} = \mu$$



It is called a potential because it goes in the direction from high to low, which is the direction of all potentials, like gravitational potential.

9. Is the mixing of different types of molecules in an ideal gas spontaneous?

Justify your answer using mathematical expressions for the chemical potential.

The mixing of different types of molecules of an ideal gas is spontaneous, as in  $\Delta G_{\text{mixing}} = nRT \sum x_i \ln x_i$ ,  $\ln x_i$  is always negative, making  $\Delta G_{\text{mixing}}$  always be negative. Since  $\Delta G_{\text{mixing}}$  is negative, this means that the mixing is spontaneous.

10. For a given chemical reaction involving only gases at equilibrium, if  $\Delta G_{\text{rxn}}^{\circ} > 0$ , will there be more product formed or more reactant? Justify your answer using one or more equations.

$K = e^{-\frac{\Delta G}{RT}}$  As  $\Delta G$  gets bigger,  $K_p$  gets smaller (less than 1), meaning that there are more reactants.

Extra credit:

Write your favourite equation from this semester & briefly explain the insight into chemistry it provides.

$\Delta S \geq 0$  Entropy is a quantity that can never decrease over time in an isolated system. This is the basis of the Second Law of Thermodynamics.

This equation is key to explaining why reactions happen one way and not another.

At the same time, I think that this idea is also visible in human behaviour. Its versatility is the reason why it is my favourite.