

Exam #2

Who did you work with?

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I did not ask anyone else for help.

1) The Decarboxylation of pyruvic acid occurs via the following rxn:

$$\text{a) } \Delta G^\circ_{\text{rxn}} = \Delta G_{\text{products}} - \Delta G_{\text{reactants}}$$

$$= (-394 - 133) - (-463)$$

$$\Delta G^\circ_{\text{rxn}} = -64 \text{ kJ/mol}$$

Yes, ~~it is~~ it is spontaneous because $\Delta G^\circ_{\text{rxn}}$ at 25°C is negative.

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

First, we find: $\Delta H^\circ_{\text{rxn}} = \sum \Delta H^\circ_{\text{products}} - \sum \Delta H^\circ_{\text{reactants}}$

$$= (-394 - 166) - (-584)$$

$$\Delta H^\circ_{\text{rxn}} = 24 \text{ kJ/mol}$$

Next, we find: $\ln K_p(298 \text{ K}) = \frac{\Delta G^\circ_{\text{rxn}}}{RT} = \frac{(-64)(10^3)}{(8.314)(298)}$

$$\ln K_p(298 \text{ K}) = \frac{0.0258}{25.83} = 25.83$$

$$\ln K_p(80 \text{ K}) = 25.83 - \left(\frac{24 \times 10^3}{8.314} \right) \left(\frac{1}{80} - \frac{1}{298} \right)$$

$$= 0.0258 - 0.026$$

$$= 25.83 - 26.40 = -0.57$$

$$\ln K_p(80 \text{ K}) = -0.57$$

$$K_p(80 \text{ K}) = 0.57$$

c) At 80 K (lower Temperature), K_p is less than 1

Thus reactants are favored at low T

2) For a pure substance

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

We know this is a Maxwell relation taken under constant temperature and volume measures so we start with the internal energy.

Since U is a state function, then

$$\left(\frac{\partial}{\partial V} \left(\frac{\partial U(V, T)}{\partial T} \right)_V \right)_T = \left(\frac{\partial}{\partial T} \left(\frac{\partial U(V, T)}{\partial V} \right)_T \right)_V$$

Substitute $\delta U = T \delta S - P \delta V$ into both sides

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

$\text{Obc } \delta V = 0 \qquad \qquad \qquad \text{Obc } \delta T = 0$

This leaves us with

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

We know that

$$\left(\frac{\delta V}{\delta P} \right)_T \left(\frac{\delta P}{\delta V} \right)_T \left(\frac{\delta T}{\delta P} \right)_V = -1$$

~~$$\beta = \frac{1}{V} \left(\frac{\delta V}{\delta P} \right)_T \quad K = -\frac{1}{V} \left(\frac{\delta P}{\delta V} \right)_T$$~~

Substituting leads to:

$$\frac{\beta}{K} = - \left(\frac{\delta P}{\delta T} \right)_V \rightarrow \left(\frac{\delta S}{\delta V} \right)_T = \left(\frac{\delta P}{\delta T} \right)_V = \frac{\beta}{K}$$

Knowing that $\delta S_m = \frac{\delta S}{n}$ we can substitute $\delta S_m \cdot n$ into the equation

$$\left(\frac{\delta S_m}{\delta V}\right)_T \cdot n = \frac{B}{K}$$

$$\left(\frac{\delta S_m}{\delta V}\right)_T = \frac{B}{nK}$$

b) Integrating both sides knowing that $\frac{B}{nK}$ is constant gives:

$$\int \delta S_m = \frac{B}{nK} \int \delta V$$

$$\Delta S_m = \frac{B}{nK} \Delta V \text{ since } \frac{B}{nK} \text{ is always (+)}$$

S_m increases with ΔV increasing

c) We start with the definition of the Gibbs free energy for 3 substances n_1, n_2, n_3

(P dependent)

$$dG = \left(\frac{\delta G}{\delta T}\right)_{P, n_1, n_2, n_3} dT + \left(\frac{\delta G}{\delta P}\right)_{T, n_1, n_2, n_3} dP +$$

(T dependent)

$$\left(\frac{\delta G}{\delta n_1}\right)_{T, P, n_2, n_3} dn_1 + \left(\frac{\delta G}{\delta n_2}\right)_{T, P, n_1, n_3} dn_2$$

(molar
dependence)

$$+ \left(\frac{\delta G}{\delta n_3}\right)_{T, P, n_1, n_2} dn_3$$

~~Since dT, dP~~ we can write

we define

$$\left(\frac{\delta G}{\delta n_x}\right)_{P, T} \text{ to be chemical potential} = \mu_i$$

Now we have

$$dG = \left(\frac{\delta G}{\delta T}\right)_{P, n_x} dT + \left(\frac{\delta G}{\delta P}\right)_{T, n_x} dP + \sum \mu_i dn_i$$

Since we are interested in volume dependence, G can also be written as

$$dG = V dP + -S dT + \sum M_i dn_i$$

When temperature & concentration ($dn_i = 0$) is constant, then isolating V :

$$V = \left(\frac{\partial G}{\partial P} \right)_{T, n_x} \quad (1) \quad (dT=0)$$

When Temperature & Pressure are constant, then isolating M_i gives:

$$M_i = \left(\frac{\partial G}{\partial n_x} \right)_{T, P} \quad (2) \quad (dT=0) \\ (dP=0)$$

We now derive both sides of equation (1) w/ regards to ~~chemical potential~~
and both sides of equation (2) w/ regards to pressure

$$(1) \quad \left(\frac{\partial V}{\partial P} \right)_{T, P} = \left(\frac{\partial^2 G}{\partial P \partial n_x} \right) \quad \text{total moles} \quad \text{equal to each other}$$

$$(2) \quad \left(\frac{\partial M_i}{\partial P} \right)_{T, n_x} = \left(\frac{\partial^2 G}{\partial n_x \partial P} \right)$$

$$\text{Thus, } \left(\frac{\partial V}{\partial n_x} \right)_{T, P} = \left(\frac{\partial M_i}{\partial P} \right)_{T, n_x}$$

d) Using the result from c), we get:

$$\left(\frac{\partial M_{COCl_2}}{\partial P} \right)_{T, n_{CO}, n_{Cl_2}} = \left(\frac{\partial V}{\partial n_{COCl_2}} \right)_{T, P, n_{CO}, n_{Cl_2}}$$

The chemical potential ($COCl_2$) increases with an increasing pressure.

Reactants will be favored since total moles conserved

At constant T & P , volume increases w/ an increase in $COCl_2$ moles

Thus,

e) At P, we have M_{CoCl_2} :

$$\left(\frac{\partial M_{\text{CoCl}_2}}{\partial P} \right)_{T, n_{\text{Co}}, n_{\text{Cl}}} = \left(\frac{\partial V}{\partial n_{\text{CoCl}_2}} \right)_{P, T, n_{\text{Co}}, n_{\text{Cl}}}$$

Integrating both sides gives:

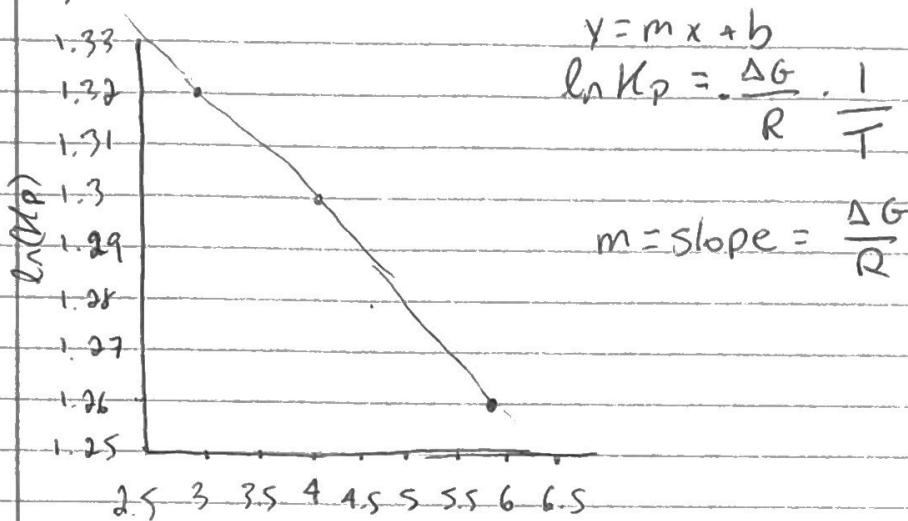
$$\int_{M_i}^{M_{\text{CoCl}_2}} dM = \left(\frac{\partial V}{\partial n_{\text{CoCl}_2}} \right) \int_{P_0}^P dP$$

$$(M_{\text{CoCl}_2} - M_i) = \left(\frac{\partial V}{\partial n_{\text{CoCl}_2}} \right) (P - P_0)$$

3) The following TD data was measured for a chem. rxn:

T	K_p	x, r
167	3.53	$(5.9 \times 10^{-3}, 1.26)$
250	3.67	$(4 \times 10^{-3}, 1.30)$
333	3.74	$(3 \times 10^{-3}, 1.32)$

a) Plot



$$b) m = \frac{\Delta y}{\Delta x} = \frac{(1.30 - 1.26)}{((4 \times 10^{-3}) - (5.9 \times 10^{-3}))} = -21.05$$

(I got -30.5
when I choose 2
other pts. close
enough)

$$-21.05 = -\frac{\Delta G^\circ}{8.314} \rightarrow \Delta G^\circ = +175 \text{ J/mol}$$

Reaction is ^{not} spontaneous because ΔG° is ~~negative~~ positive

c) It is enthalpically driven as the reaction is the following when

$$\frac{d \ln K_p}{dT} = -\frac{\Delta H^\circ}{R T^2} \xrightarrow{\text{enthalpy}} \text{deriving with respect to temperature}$$

no Entropy

Short Answers

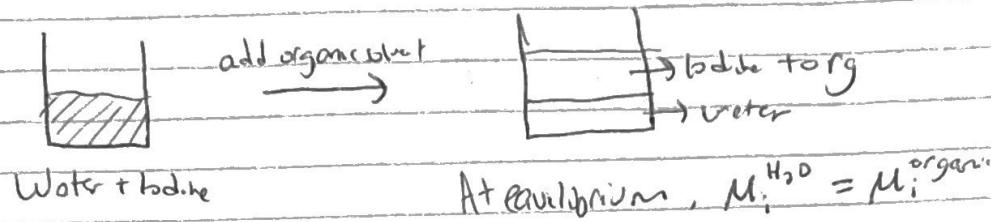
- 4) The 2nd Law of Thermodynamics states that it is impossible for a system to undergo a cyclic process whose side effects are the flow of heat into the system from a heat reservoir, & the performance of an equal amount of work by the system on the surroundings ~~exotherm~~. In other ~~heat~~ words, the efficiency is always less than 100%.
- 5) The 3rd Law of Thermodynamics states that entropy of a pure, crystalline substance (elemental or compounds) is 0 at 0K. $S=0$ at 0K.
This makes it different than internal energy and enthalpy because we can use $S=0$ at 0K as a reference state to find the entropy at the desired temperature. The same cannot be done with U and H since the reference state ~~at 0K~~ is unknown.
- 6) We cannot build a perpetual motion machine because it violates the 2nd law of TD. ~~The total work done by~~ The total work done by the machine will always be less than the heat absorbed, making the efficiency less than 100%, thus not perpetual.
- 7) The Gibbs free energy ~~is~~ is more applicable to chemists because it is a measurable quantity that tells us the amount of energy that can do work in a system, which is used to tell whether a reaction is spontaneous or not. As opposed to the Helmholtz free energy which tells us about the maximum energy that can be extracted from a closed system, which is not as directly related to chemical reactions.

8) Chemical Potential:

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

(Pressure, temp, & concentration const)

It is a potential because the direction that drives chemical potential is from high to low. Similar to gravitational Potential Energy where objects tend to fall from high to low potential energy. For this reason, it is appropriate to term chemical potential as a potential.



Q) We'll take two ideal gases a and b for simplification.
We start with the free energy before mixing:

$$G_i = G_a + G_b = n_a G_{m,a} + n_b G_{m,b}$$

Now we consider the free energy where both components are dispersed in mixture:

$$G_F = n_a (G_{m,a} + RT \ln x_a) + n_b (G_{m,b} + RT \ln x_b)$$

We know that $\Delta G_{\text{mix}} = G_F - G_i$ (difference in free energy states of mix.)

$$\Delta G_{\text{mix}} = RT n_a \ln x_a + RT n_b \ln x_b$$

$x_a, x_b < 1$ molality $\Delta G_{\text{mix}} < 0$. Reaction spontaneous

10) we know that $\Delta G_m^\circ = \Delta H - T\Delta S$
 $(>0) \quad (>0)$

If $\Delta G_m^\circ > 0$, then $\Delta H > T\Delta S$
(if $\Delta H > 0 \Rightarrow \Delta S < 0$)

then the reaction is not spontaneous and more reactants will be formed.

Extra Credit:

1) The equation of the 1st law of TD

$$\Delta U = Q + W$$

It is a very simple equation that can be derived in many multiple ways to allow us to study systems in very advanced ways.