

CH302H HW Week 6, key

$$1. a) \Delta G_{rxn}^{\circ} = \sum_{prod} \nu \Delta G_f^{\circ} - \sum_{react.} \nu \Delta G_f^{\circ}$$

$$= \Delta G_f^{\circ}(\text{CHCl}_3(g)) + 3\Delta G_f^{\circ}(\text{HCl}(g)) - \Delta G_f^{\circ}(\text{CH}_4(g)) - 3(\Delta G_f^{\circ}(\text{Cl}_2(g)))$$

$$= -73.7 \text{ kJ/mol} + 3(-95.3 \text{ kJ/mol}) - (-50.7 \text{ kJ/mol}) - 0$$

$$\Delta G_{rxn}^{\circ} = -309 \text{ kJ/mol}$$

b) need to know if $\Delta G_{rxn} < 0$ @ 500k $\Rightarrow \Delta G_{rxn} = \Delta H_{rxn} - T\Delta S_{rxn} < 0$?

$$\Delta H_{rxn}^{\circ} = \Delta H_f^{\circ}(\text{CHCl}_3(l)) + 3\Delta H_f^{\circ}(\text{HCl}(g)) - \Delta H_f^{\circ}(\text{CH}_4(g)) - 3\Delta H_f^{\circ}(\text{Cl}_2(g))$$

$$= -135.44 \text{ kJ/mol} + 3(-92.3 \text{ kJ/mol}) - (-74.8 \text{ kJ/mol}) - 0$$

$$\Delta H_{rxn}^{\circ} = -337.6 \text{ kJ/mol}$$

$$\Delta S_{rxn}^{\circ} = S_m^{\circ}(\text{CHCl}_3(l)) + 3S_m^{\circ}(\text{HCl}(g)) - S_m^{\circ}(\text{CH}_4(g)) - 3S_m^{\circ}(\text{Cl}_2(g))$$

$$= 216.4 \text{ J/kmol} + 3(186.9 \text{ J/kmol}) - 186.3 \text{ J/kmol} - 3(223.0 \text{ J/kmol})$$

$$\Delta S_{rxn}^{\circ} = -78.2 \text{ J/kmol}$$

(which makes sense because we are losing 1 mol of gas)

Assume these are constant @ T=500k

$$\Delta G_{rxn} = -337.6 \text{ kJ/mol} - (500 \text{ k})(-0.0782 \text{ kJ/mol})$$

$$\boxed{\Delta G_{rxn} = -298.3 \text{ kJ/mol}} \Rightarrow \text{spontaneous @ } T=500\text{k}$$

But because $\Delta S < 0$, increasing T will decrease k. You should ask yourself @ what T will this rxn. no longer be spontaneous?

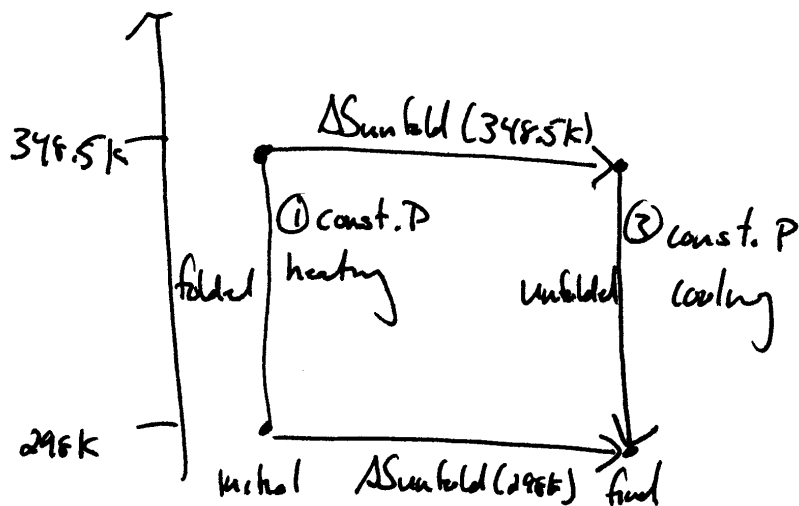
2. $\Delta S_{\text{unfold}}(298\text{K})$ from $\Delta S_{\text{unfold}}(348.5\text{K})$

(2)

$$\Delta H_{\text{unfold}} = 509 \text{ kJ/mol} \quad @ \quad 348.5 \text{ K}$$

assume $C_p(\text{unfolded}) = \text{constant}$

$$C_p(\text{unfolding}) = C_p(\text{folded}) = 6.28 \text{ kJ/mol K}$$



$$\Delta S_{\text{unfold}} = \Delta S_{\text{heat}} + \Delta S_{\text{unfold}}(348.5\text{K}) + \Delta S_{\text{cool}}$$

$$\textcircled{1} \Delta S_{\text{heat}} = C_p \ln\left(\frac{T_f}{T_i}\right) = C_{p,m} \ln\left(\frac{348.5\text{K}}{298\text{K}}\right)$$

$$\Delta S_{\text{heat}} = C_{p,m} (0.157)$$

$$\textcircled{2} \Delta S_{\text{unfold}}(348.5\text{K}) = \frac{\Delta H_{\text{unfold}}}{T_{\text{unfold}}} = \frac{509 \text{ kJ/mol}}{348.5\text{K}} = 1.46 \text{ kJ/mol K}$$

$$\textcircled{3} \Delta S_{\text{cool}} = C_{p,m} \text{unfolded} \ln\left(\frac{T_f}{T_i}\right) = (C_{p,m} + 6.28 \text{ kJ/mol K}) \ln\left(\frac{298\text{K}}{348.5\text{K}}\right)$$

$$\Delta S_{\text{cool}} = C_{p,m} (-0.157) - 0.963 \text{ kJ/mol K}$$

$$\Delta S_{\text{unfold}} = C_{p,m} (-0.157) - 0.963 \text{ kJ/mol K} + 1.46 \text{ kJ/mol K} + C_{p,m} (0.157)$$

$$\Delta S_{\text{unfold}} = 477 \text{ J/mol K} @ 298 \text{ K}$$

3. $\Delta H_{vap}^{\circ} = 30.7 \text{ kJ/mol}$ $T_{vap} = 80.1^{\circ}\text{C} = 353.1 \text{ K}$

$\Delta G_{vap} = \Delta H_{vap} - T\Delta S_{vap}$

@ $T = 353.1 \text{ K}$, $\Delta G_{vap} = \Delta G_{vap}^{\circ} = 0$

$\Delta G_{vap} = \Delta H_{vap} - T\Delta S_{vap}$

$\Delta S_{vap}^{\circ} = \frac{\Delta H_{vap}^{\circ}}{T_{vap}} = \frac{30.7 \times 10^3 \text{ J/mol}}{353.1 \text{ K}}$

$\Delta S_{vap}^{\circ} = 86.9 \text{ J/kmol}$

assume this is constant.

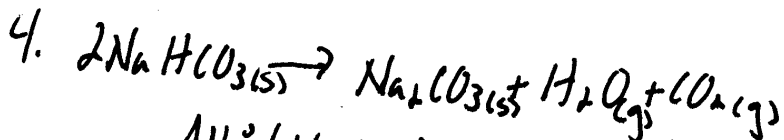
@ $T = 348.1 \text{ K}$

$\Delta G_{vap} = (30.7 \times 10^3 \text{ J/mol}) - (348.1 \text{ K})(86.9 \text{ J/kmol}) = 441 \text{ J/mol}$

@ $T = 358.1 \text{ K}$

$\Delta G_{vap} = (30.7 \times 10^3 \text{ J/mol}) - (358.1 \text{ K})(86.9 \text{ J/kmol}) = -428 \text{ J/mol}$

* for this problem, pay close attention to what is standard state (°) + what unit.



$\Delta H_f^{\circ}(\text{NaHCO}_3) = -950.8 \text{ kJ/mol}$

$\Delta H_f^{\circ}(\text{Na}_2\text{CO}_3) = -1130.7 \text{ kJ/mol}$

$\Delta H_f^{\circ}(\text{H}_2\text{O}) = -241.8 \text{ kJ/mol}$

$\Delta H_f^{\circ}(\text{CO}_2) = -393.5 \text{ kJ/mol}$

$S_m^{\circ}(\text{NaHCO}_3) = 101.7 \text{ J/kmol}$

$S_m^{\circ}(\text{Na}_2\text{CO}_3) = 135.0 \text{ J/kmol}$

$S_m^{\circ}(\text{H}_2\text{O}) = 188.7 \text{ J/kmol}$

$S_m^{\circ}(\text{CO}_2) = 213.6 \text{ J/kmol}$



$$a) \Delta H_{rxn}^{\circ} = \Delta H_f^{\circ}(\text{Na}_2\text{CO}_3) + \Delta H_f^{\circ}(\text{H}_2\text{O}) + \Delta H_f^{\circ}(\text{CO}_2) - 2\Delta H_f^{\circ}(\text{NaHCO}_3) \quad (1)$$

$$= -1130.7 \text{ kJ/mol} + -241.8 \text{ kJ/mol} + -393.5 \text{ kJ/mol} - 2(-950.8 \text{ kJ/mol})$$

$$\Delta H_{rxn}^{\circ} = 135.6 \text{ kJ/mol}$$

* does this # make sense based on the info you have been given in the problem?

Be sure to justify this to yourself.
(assume constant)

$$\Delta S_{rxn}^{\circ} = S_m^{\circ}(\text{Na}_2\text{CO}_3) + S_m^{\circ}(\text{H}_2\text{O}) + S_m^{\circ}(\text{CO}_2) - 2(S_m^{\circ}(\text{NaHCO}_3))$$

$$= 135.0 \text{ J/kmol} + 188.7 \text{ J/kmol} + 213.6 \text{ J/kmol} - 2(101.7 \text{ J/kmol})$$

$$\Delta S_{rxn}^{\circ} = 333.9 \text{ J/kmol}$$

* again, make sure the magnitude of this # makes sense to you.
(assume constant)

$$\Delta G_{rxn}^{\circ} = \Delta H_{rxn}^{\circ} - T\Delta S_{rxn}^{\circ} = 135.6 \times 10^3 \text{ J/mol} - (298 \text{ K})(333.9 \text{ J/kmol})$$

$$\Delta G_{rxn}^{\circ} = 36.1 \text{ kJ/mol}$$

@ 298 K!

But, since $\Delta S_{rxn}^{\circ} \gg 0$, we expect that as T increases, ΔG_{rxn}° becomes a smaller number and will eventually cross 0.

$$@ T = 150^{\circ}\text{C} = 423 \text{ K}: \Delta G_{rxn} = \Delta H_{rxn}^{\circ} - T\Delta S_{rxn}^{\circ} = (135.6 \times 10^3 \text{ J/mol}) - (423 \text{ K})(333.9 \text{ J/kmol})$$

$$\Delta G_{rxn}(423 \text{ K}) = -5.64 \text{ kJ/mol}$$

$$K_p = \exp\left[\frac{-\Delta G_{rxn}}{RT}\right] = \left[\frac{-(-5.64 \times 10^3 \text{ J/mol})}{(8.314 \text{ J/kmol})(423 \text{ K})}\right] = 1.60 = K_p$$

b) $K_p = P(H_2O)P(O_2)$

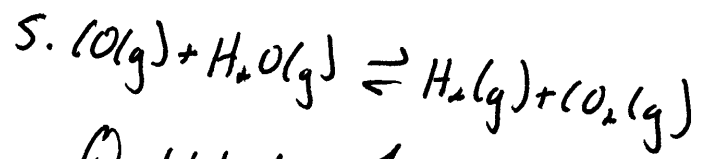
$P(O_2) = 0.8 \text{ atm}$

$K_p = 1.60$

$P(H_2O) = \frac{K_p}{P(O_2)} = \frac{1.60}{0.8 \text{ atm}}$

$P(H_2O) = 2.0 \text{ atm}$

(remember there is a P° in the denominator of both partial pressure terms to make units work out).

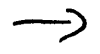


Qualitatively: There are equal moles of gas on each side of the equation, so nothing happens when you increase pressure

Quantitatively:
$$K_p = \frac{\left(\frac{P_{H_2}}{P^\circ}\right)^{\nu_{H_2}} \left(\frac{P_{CO_2}}{P^\circ}\right)^{\nu_{CO_2}}}{\left(\frac{P_{CO}}{P^\circ}\right)^{\nu_{CO}} \left(\frac{P_{H_2O}}{P^\circ}\right)^{\nu_{H_2O}}}$$

but $P_{H_2O} = X_{H_2O} P_{TOT}$
 $P_{CO_2} = X_{CO_2} P_{TOT}$
etc...

$$\Rightarrow K_p = \frac{\left(\frac{X_{H_2} P_{TOT}}{P^\circ}\right)^{\nu_{H_2}} \left(\frac{X_{CO_2} P_{TOT}}{P^\circ}\right)^{\nu_{CO_2}}}{\left(\frac{X_{CO} P_{TOT}}{P^\circ}\right)^{\nu_{CO}} \left(\frac{X_{H_2O} P_{TOT}}{P^\circ}\right)^{\nu_{H_2O}}}$$



$$\text{define } K_x = \frac{X_{H_2}^{v_{H_2}} X_{CO_2}^{v_{CO_2}}}{X_{CO}^{v_{CO}} X_{H_2O}^{v_{H_2O}}} = \prod_c X_c^{v_c}$$

$$K_p = K_x \left(\frac{P_{\text{Tot}}}{p^0} \right)^{v_{H_2} + v_{CO_2} - v_{CO} - v_{H_2O}} = K_x \left(\frac{P_{\text{Tot}}}{p^0} \right)^{+1-1-1} = K_x \frac{P_{\text{Tot}}}{p^0}$$

$$\underline{K_p = 1(K_x)}$$

No change in K_x is necessary to keep K_p constant, so nothing happens as pressure increases.

$$6. \quad k_p(2100\text{K}) = 2k_p(2000\text{K})$$

$$\ln\left(\frac{k_p(2100\text{K})}{k_p(2000\text{K})}\right) = \frac{-\Delta H_{rxn}^\circ}{R} \left(\frac{1}{2100\text{K}} - \frac{1}{2000\text{K}} \right)$$

$$\text{Solve for } \Delta H_{rxn}^\circ = \frac{-R \ln\left(\frac{k_p(2100\text{K})}{k_p(2000\text{K})}\right)}{\left(\frac{1}{2100\text{K}} - \frac{1}{2000\text{K}}\right)} = \frac{(-8.314 \text{ J/mol}) \ln(2)}{\left(\frac{1}{2100\text{K}} - \frac{1}{2000\text{K}}\right)}$$

$$\Delta H_{rxn}^\circ = 242 \text{ kJ/mol}$$