

UWO **CHEM 1302**

Winter 2024, Chapter 6 Notes



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6.1 Gibbs Free Energy + Spontaneity

6.1.1

Gibbs Free Energy and Spontaneity

- It is not always convenient to calculate the entropy of the system and the surroundings to determine whether a process is spontaneous
- Gibbs showed that at constant T and p another state function, ΔG , of the system can predict whether a reaction is spontaneous or not.

- under constant T:

$$\begin{array}{c} \text{Gibbs} \\ \text{Free Energy} \\ \Delta G = \Delta H - T\Delta S \end{array}$$

- under constant T and P:
- If $\Delta G > 0$ the reaction is non-spontaneous (spontaneous in the reverse direction)
- If $\Delta G < 0$ the reaction is spontaneous and reversible ~~irreversible~~ irreversible
- Just like enthalpy and entropy Gibbs free energy for a reaction can be calculated

$$\Delta G_{products} - \Delta G_{reactants} = \Delta G_{rxn}$$

Note: we can use the same equation we saw for enthalpy of the reaction and entropy of the reaction.
For Gibbs Free Energy just be aware that if the tables are given with values at 25C, this equation
can only be used when reaction conditions are at 25C!

- Gibbs free energy is a state function which allows us to set up the following relation

$$\Delta G_{forward} = -\Delta G_{reverse}$$

- Also recall how for ΔH°_f of aqueous ions, it was not possible to separate the cation and anion contributions
 - $\Delta H^\circ_f = 0$ for H^+
 - we can do the same for entropy and Gibbs free energy: $\Delta S^\circ_f = 0$ for H^+ and $\Delta G^\circ_f = 0$ for H^+

6.1.2

Spontaneity

Look at each row in the following table, use $\Delta G = \Delta H - T\Delta S$

Which are spontaneous, which are not?

Which are spontaneous only at a high/low temperature?

If we change the temperature, which could become non-spontaneous??

Which one is entropy driven to be spontaneous and which one is enthalpy driven to be spontaneous?

ΔG	ΔH	ΔS
-	-	+
-	-	-
-	+	+
+	+	-'

We can be even more specific with our temperatures, rather than saying high or low temperatures to be spontaneous:

Write a < or > sign:

For Row 2: $T \frac{\Delta H}{\Delta S}$

For Row 3: $T \frac{\Delta H}{\Delta S}$

Now what if for row 2 we had placed the opposite sign?

What about for row 3 if we placed the opposite sign?

6.1.3

Using the following table, predict which of the following reactions would be spontaneous at 25°C:

	ΔH	ΔS
Reaction 1:	$9.25 \frac{kJ}{mol}$	$25.1 \frac{J}{molK}$
Reaction 2:	$2.85 \frac{kJ}{mol}$	$-125 \frac{J}{molK}$

$$T = 25^\circ C = 298 K$$

If either of the reactions is non-spontaneous, at what temperature might it become spontaneous?

Consider reaction 1:

Now consider reaction 2:

$$\begin{aligned} \text{Rxn 1: } \Delta G &= \Delta H - T\Delta S \\ &= 9250 - 298(25.1) \\ &= 1770.2 \text{ J/mol} \end{aligned}$$

$\Delta G > 0$ non-spontaneous $\Rightarrow T$ need higher.

$$\frac{\Delta H}{\Delta S} = \frac{9250}{25.1} = 368.5 K$$

$$\begin{aligned} \text{Rxn 2: } \Delta G &= \Delta H - T\Delta S \\ &= 2850 - 298(-125) \\ &= 2850 + 37250 \\ &= 40100 \text{ J/mol} \end{aligned}$$

$\Delta G > 0$ non-spontaneous

\therefore Both ΔH & $-T\Delta S$ is always positive no matter what temperature, the rxn is always non-spontaneous.

Predicting Spontaneity from Entropy

- There are two main ways you may be asked to figure out the spontaneity of a process
 - If you are given the change in entropy, temperature, AND change in enthalpy (ΔH)
 - If you are given the change in entropy of the system AND the change in entropy of the surroundings (from the 2nd law of thermodynamics)
 - Remember $\Delta S_{universe}$ allows us to predict spontaneity and $\Delta S_{universe} = \Delta S_{system} + \Delta S_{surr}$

 EXAM TIP

This chart can be used to predict the spontaneity of a process if you're only given the change in entropy of the system and surroundings

ΔS_{system}	$\Delta S_{surroundings}$	Is it spontaneous?
+	+	spontaneous
-	-	non-spontaneous
-	+	depends on the magnitude of each
+	-	depends on the magnitude of each
$\Delta S_{universe} = 0$		Equilibrium

6.2

Connecting Gibbs Free Energy and Equilibrium

6.2.1

Chemical Equilibrium and ΔG

- In general the Gibbs free energy can be related to the reaction quotient by the following expression

$$\Delta G = \Delta G^\circ + RT \ln Q$$

Recall:

$\Delta G < 0$ for a spontaneous process
 $\Delta G = 0$ at equilibrium

- If the reaction is at equilibrium then:

$$\begin{aligned}\Delta G &= 0 & Q &= K \\ && \therefore \\ \Delta G^\circ &= -RT \ln K\end{aligned}$$

We can rearrange this equation to solve for K:

$$\ln K = \frac{\Delta G^\circ}{-RT}$$

$$e^{\ln K} = e^{\left(\frac{\Delta G^\circ}{-RT}\right)}$$

$$\ln e(K) = e^{\left(\frac{\Delta G^\circ}{-RT}\right)}$$

$$K = e^{\left(\frac{\Delta G^\circ}{-RT}\right)}$$

i WIZE TIP

We just covered 3 important equations to know for your exam!

1)

$$\Delta G = \Delta G^\circ + RT \ln Q$$

2) Is what we get when we let $\Delta G=0$ in the above equation:

$$\Delta G^\circ = -RT \ln K$$

3) We get when we solve for K using equation 2:

$$K = e^{\left(\frac{\Delta G^\circ}{RT}\right)}$$

Note: the e in the above equation is a button on your calculator! We will look at some problems so you can get some practice getting familiar with that button!

Gibbs Free Energy and Chemical Reactions

Gibbs free energy is a state function, so just like enthalpy we can use Gibbs free energies of formation to determine the change in Gibbs free energy for a reaction. This equation can only be used when the temperature is 298K!

$$\Delta_r G^\circ = \sum_i v_i \Delta_f G_{m,i}^\circ (\text{products}) - \sum_j v_j \Delta_f G_{m,j}^\circ (\text{reactants})$$

van't Hoff Equation

$$\ln \left(\frac{K_2}{K_1} \right) = \frac{-\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

**memorize this equation as well!

6.2.2

DeltaG° and K

If $\Delta G^\circ < 0$ then K is...

$$K > 1$$

If $\Delta G^\circ > 0$ then K is...

$$0 < K < 1$$

If $\Delta G^\circ = 0$ then K is...

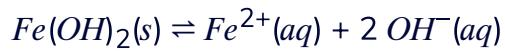
$$K = 1$$

Note: that ΔG° does not determine spontaneity (remember ΔG does!) ΔG° only tells us about the value of K

- only when $Q=1$ or everything is in standard state, or everything is in standard state, will ΔG° tell us about spontaneity

6.2.3

Consider the following reaction at 25°C:



Calculate ΔG° for the reaction. K_{sp} for $Fe(OH)_2$ is 1.6×10^{-14} .

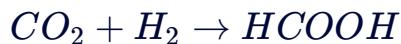
$$\Delta G^\circ = -RT \ln K$$

$$\Delta G^\circ = - (8.314)(298) \ln (1.6 \times 10^{-14})$$

$$\Delta G^\circ = 78.7 \text{ kJ/mol}$$

6.2.4

ΔrS° and ΔrH° are known to be $-225.3 \text{ J K}^{-1} \text{ mol}^{-1}$ and $-32.8 \text{ kJ mol}^{-1}$ respectively for the following reaction.



- Is this reaction spontaneous under standard conditions at $T = 298\text{K}$ and $P = 1 \text{ atm}$?
- Are reactants or products favoured in the above conditions?
- At what temperature does the reaction favour the opposite?

a.) $\Delta G = \Delta H - T\Delta S$
 $= -32800 - 298(-225.3)$

$\Delta G = 34 \text{ kJ/mol} \Rightarrow$ not spontaneous

b) since the ΔG° is positive it means that reactants are favored over the product under standard condition.

c) A reaction transitions from reactants to product when $\Delta G^\circ = 0$

$\Delta G^\circ > 0 \Rightarrow$ reactants are favored, $\Delta G^\circ < 0 \Rightarrow$ product are favored.

$$\Delta G^\circ = 0 = \Delta H^\circ - T\Delta S^\circ$$

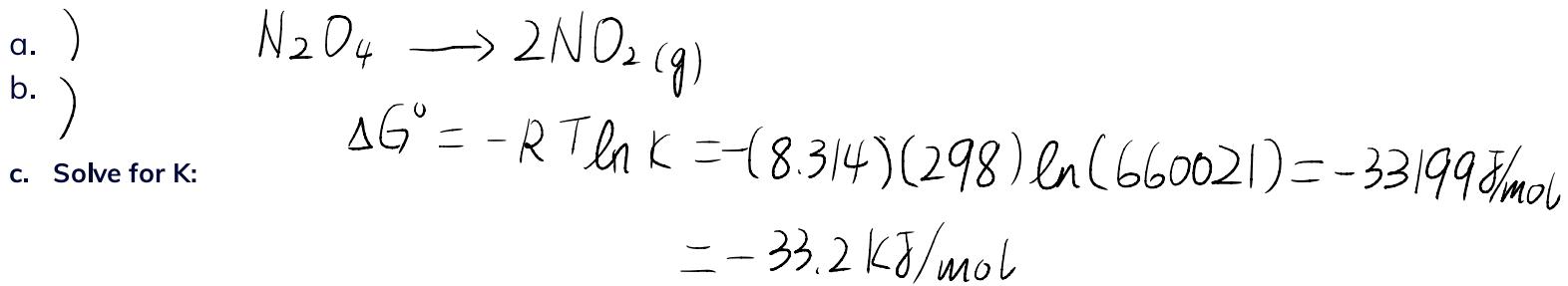
$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{-32800}{-225.3} = 145.6 \text{ K}$$

\therefore Any temperature below $145.6 \text{ K} \Rightarrow \Delta G < 0 \Rightarrow$ spontaneous

6.2.5

The equilibrium constant for the decomposition of $\text{N}_2\text{O}_4(\text{g})$ into $\text{NO}_2(\text{g})$ has an equilibrium constant $K = 660021$ at 298K.

- Write the balanced chemical reaction for the decomposition of $\text{N}_2\text{O}_4(\text{g})$.
- What is ΔG° for the above reaction?
- It is known that $\Delta S^\circ = +165 \text{ J mol}^{-1} \text{ K}^{-1}$ and $\Delta H^\circ = +15.9 \text{ kJ mol}^{-1}$. Assuming ΔH° and ΔS° are temperature independent, calculate the equilibrium constant, K.



$$\begin{aligned} c) \quad \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= 15900 \text{ J/mol} - 298 \text{ K}(165 \text{ J/mol}\cdot\text{K}) \end{aligned}$$

$$\Delta G^\circ = -33270 \text{ J/mol}$$

$$\Delta G^\circ = -RT \ln K$$

$$\ln K = \frac{\Delta G^\circ}{-RT}$$

$$e^{\ln K} = e^{\frac{\Delta G^\circ}{-RT}} \quad \ln e = 1$$

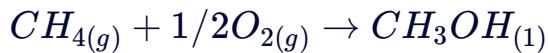
$$K = e^{\frac{\Delta G^\circ}{-RT}} = e^{-\frac{-33270}{8.314 \times 298}}$$

$$K = e^{13.428}$$

$$K = 679063$$

6.2.6

In British Columbia there has been fierce debate over whether we should increase or halt production of LNG liquefied natural gas (CH_4). One alternative to liquefying CH_4 (bp = -161.5°C) is to convert it directly into methanol (CH_3OH) which is a liquid at room temperature and pressure in the reaction shown below.



Substance	$\Delta H_{f,m}^\circ (\text{kJ mol}^{-1})$	$S_{f,m}^\circ (\text{J mol}^{-1})$
$\text{CH}_{4(g)}$	-74.8	186
$\text{O}_{2(g)}$		205
$\text{CH}_3\text{OH}_{(l)}$	-238.7	126.8

- Calculate ΔH° , ΔS° and ΔG° at 25°C for the conversion of natural gas to methanol. Is this process spontaneous?
- Calculate the equilibrium constant for this reaction at 25°C .
- What are three things you could do to favour the production of methanol?
- Under the following conditions is the reaction spontaneous? (see below)

$$a) \Delta H^\circ = \Delta H_f^{\circ(\text{reactants})} - \Delta H_f^{\circ(\text{products})}$$

$$= -238.7 - (-78.7) = -163.9 \text{ kJ/mol}$$

$$c) \Delta S^\circ = \Delta S_f^{\circ(\text{products})} - \Delta S_f^{\circ(\text{reactants})}$$

$$= 126.8 \text{ J/mol K} - [186 \text{ J/mol K} + 0.5(205 \text{ J/mol K})] = -167 \text{ J/mol K}$$

$$\begin{aligned} d) \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= -163900 - 298(161.7) \\ &= -115713.4 \text{ J/mol} \end{aligned}$$

d. ΔG° is negative, the rxn is spontaneous

$$T = 1000\text{K} \quad b) K = e^{\frac{-\Delta G}{RT}} = e^{\frac{-115713.4}{8314.45 \times 1000}} = 1.92 \times 10^{20}$$

$$= -178.9 \text{ kJ/mol}$$

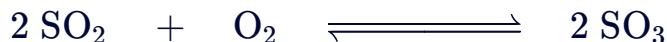
$\Delta G < 0$, the rxn is spontaneous in forward direction.

- $p(\text{O}_2) = 100\text{atm}$ c) i) increase partial pressure of CH_4 or O_2
 $p(\text{CH}_4) = 200\text{atm}$ ii) remove methanol from the rxn as formed
 $p(\text{CH}_3\text{OH}) = 1\text{atm}$ iii) cool the rxn down
iv) Increase Total Pressure/ Decrease Total Volume

**MARK YOURSELF QUESTION**

Try the problem yourself, and check the solutions to see how you did. Then mark yourself right or wrong.

Consider the following reaction



$$\Delta H^\circ = -180 \text{ kJ/mol}$$

K is measured to be 9.9×10^2 at 800 K , what temperature would the reaction need to be run at to get an equilibrium constant of 1×10^6 ?

Vant Hoff equation $\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

Given: $K_1 = 9.9 \times 10^2$ at $T_1 = 800 \text{ K}$.

$$K_2 = 1 \times 10^6$$

$$\Delta H^\circ = -180 \text{ kJ/mol} = -180,000 \text{ J/mol}$$

$$\ln\left(\frac{K_1}{K_2}\right) = \ln\left(\frac{9.9 \times 10^2}{1 \times 10^6}\right) \approx -6.919$$

$$\frac{1}{T_2} = \frac{1}{800} - \frac{8.314}{-180,000} \times 6.919$$

$$\begin{aligned} \frac{1}{T_2} &= 0.00125 + 0.000319 \\ &= 1.569 \times 10^{-3} \end{aligned}$$

$$T_2 = \frac{1}{1.569 \times 10^{-3}} = 637 \text{ K}$$

\therefore The temperature T_2 required for equilibrium constant to be 1×10^6 is approximately 637 K .