N7 - THERMODYNAMICS

Gibbs Free Energy

Now it is time for some math!

Yay!

Gibbs Free Energy

Gibbs free energy, _G_ - the maximum amount of work energy that can be released to the surroundings by a system for a constant temp and pressure system.

Gibbs free energy is often called the **chemical potential** because it is similar to the storing of energy in a mechanical system.

Gibbs Free Energy

It can be shown that:

$$-T\Delta S_{\text{univ}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}}$$

This turns into…

Gibbs Free Energy

It can be shown that:

$$-T\Delta S_{univ} = \Delta H_{sys} - T\Delta S_{sys}$$

This turns into…

Gibbs Free Energy

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

Important Equation!!!

Gibbs Free Energy

$$-T\Delta S_{univ} = \Delta H_{sys} - T\Delta S_{sys}$$

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

- Because ΔS_{univ} determines if a process is spontaneous, ΔG also determines spontaneity.

- ΔS_{univ} is positive when spontaneous, so ΔG is negative.

Gibbs Free Energy

A process will be spontaneous when ΔG is negative

Important fact that lets us do a lot of math!

Mental Math with Gibbs Free Energy

It is very common for them to ask you to predict if a reaction is spontaneous based on just the algebraic sign on ΔH and ΔS

You need to use the Gibbs equation to see if ΔG ends up + or -

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

Mental Math with Gibbs Free Energy

$\Delta H_{sys} - T\Delta S_{sys} = \Delta G_{sys}$			
ΔH	ΔS	ΔG	At…
− *exothermic*	**+** *more disorder*	**−** *ALWAYS spont.*	Any temperature
(Negative #) − $_{any}$T(Positive #) = Always Negative #			

Remember T is in Kelvin, always a positive number

Mental Math with Gibbs Free Energy

$\Delta H_{sys} - T\Delta S_{sys} = \Delta G_{sys}$			
ΔH	ΔS	ΔG	At...
+ *endothermic*	**–** *less disorder*	**+** *NEVER spont.*	Any temp
(Positive #) – $_{any}$T(Negative #) = Always Positive #			
Notice the double negative! → (Positive #) + (Positive #)			

Mental Math with Gibbs Free Energy

$\Delta H_{sys} - T\Delta S_{sys} = \Delta G_{sys}$			
ΔH	ΔS	ΔG	At…
+ *endothermic*	**+** *more disorder*	**–** *spont.*	High Temp
(Positive #) – $_{large}$T(Positive #) = Negative # *ΔH needs to be a smaller positive number than TΔS_{sys}* **Small # - Big # = Negative #** $\Delta H < T\Delta S_{sys}$			

Mental Math with Gibbs Free Energy

$\Delta H_{sys} - T\Delta S_{sys} = \Delta G_{sys}$			
ΔH	ΔS	ΔG	At…
– *exothermic*	**–** *less disorder*	**–** *spont.*	Low Temp
(Negative #) – $_{small}$T(Negative #) = Negative # **Notice the double negative! → (Negative #) + (Positive #)** *ΔH needs to be a larger negative than* TΔS_{sys} $\Delta H < T\Delta S_{sys}$			

<u>Mental Math with Gibbs Free Energy</u>

This always makes my brain feel scrambled… figure out what works for you.

- Flat out memorize it *(best, fastest)*

- Write out the equation and +/- and walk through the mental math each time *(what I do because I'm lazy, and I'm not taking timed tests like you are – ha!)*

- Find/make a mnemonic? *(Tell me if you find a good one!)*

YOU CANT LET YOUR BRAIN SHUT DOWN
Don't let it feel confused and shut off…
just walk through it slowly…

$\Delta H_{sys}-T\Delta S_{sys} = \Delta G_{sys}$			
ΔH	ΔS	ΔG	At…
− *exothermic*	**+** *more disorder*	**−** *ALWAYS spont.*	Any temp
+ *endothermic*	**−** *less disorder*	**+** *NEVER spont.*	Any temp
− *exothermic*	**−** *less disorder*	**−** *spont.*	Low Temp
− *exothermic*	**−** *less disorder*	**+** *NOT spont.*	High Temp
+ *endothermic*	**+** *more disorder*	**−** *spont.*	High Temp
+ *endothermic*	**+** *more disorder*	**+** *NOT spont.*	Low Temp

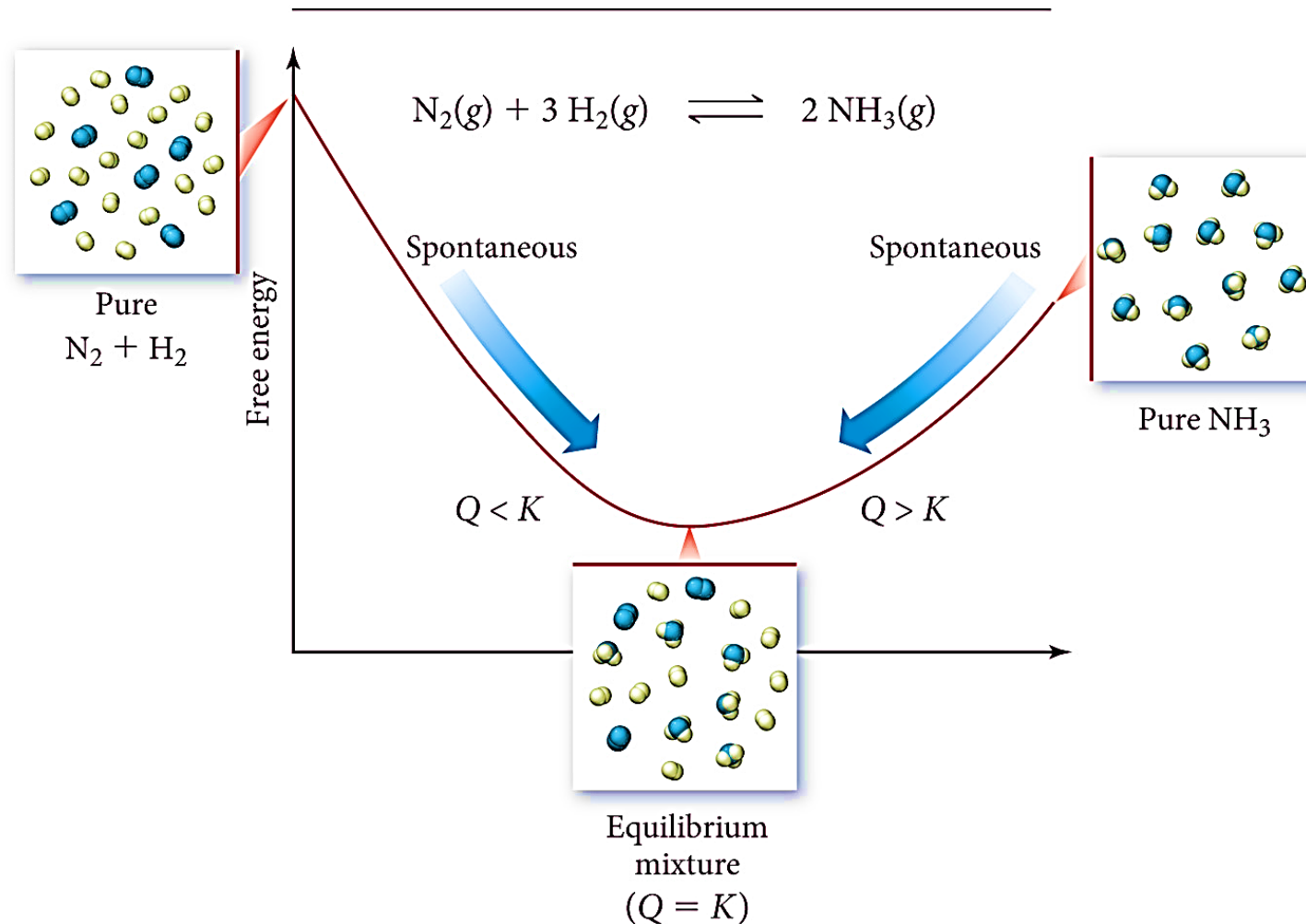|	$\Delta H < 0$	$\Delta H > 0$
$\Delta S > 0$	Spontaneous at all T ($\Delta G < 0$)	Spontaneous at high T (when $T\Delta S$ is large)
$\Delta S < 0$	Spontaneous at low T (when $T\Delta S$ is small)	Non-spontaneous at all T ($\Delta G > 0$)

So many versions online, find one you like! If you find a good one, always share with me! ☺

Gibbs at Equilibrium

When $\Delta G = 0$
the reaction is at **equilibrium**.

Gibbs at Equilibrium

Gibbs Free Energy Determines the Direction of Spontaneous Change

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Pure
$N_2 + H_2$

Free energy

Spontaneous

Spontaneous

$Q < K$

$Q > K$

Pure NH_3

Equilibrium
mixture
$(Q = K)$

Calculating Free Energy

Method #1 - **Gibbs-Helmohotz Equation**

$$\Delta G° = \Delta H° - T\Delta S°$$

For reactions at a constant temperature

Calculating Free Energy

Method #2 - A variation of Hess's Law

$C_{diamond}(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta G^0 = -397$ kJ

$C_{graphite}(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta G^0 = -394$ kJ

$C_{diamond}(s) + \cancel{O_2(g)} \rightarrow \cancel{CO_2(g)}$ $\Delta G^0 = -397$ kJ

$\cancel{CO_2(g)} \rightarrow C_{graphite}(s) + \cancel{O_2(g)}$ $\Delta G^0 = +394$ kJ

$C_{diamond}(s) \rightarrow C_{graphite}(s)$ $\Delta G^0 = -3$ kJ

Calculating Free Energy

Method #3- Standard Free Energy of Formations

$$\Delta G^0 = \sum n_p \Delta G^0_{f\,(\text{products})} - \sum n_r \Delta G^0_{f\,(\text{reactants})}$$

ΔG_f^0 of an element in its standard state is zero

Free Energy and Pressure

- Enthalpy, H, is <u>not</u> pressure dependent
- Entropy, S – <u>yes</u> pressure dependent
  - Depends on volume, so also depends on pressure
- So Gibbs will change because S changes

$$S_{\text{large volume}} > S_{\text{small volume}}$$

$$S_{\text{low pressure}} > S_{\text{high pressure}}$$

Free Energy and Equilibrium

$$\Delta G = \Delta G^{\circ} + RTLn(Q),$$

Where ΔG is at some non standard condition, and ΔG^0 is standard 1 atm, Q is some condition not at equilibrium

Remember – K = equilibrium, Q = not at equilibrium
K = Q at equilibrium

Free Energy and Equilibrium

Equilibrium point occurs at the lowest value of free energy available to the reaction system

At equilibrium: $\Delta G = 0$ and $Q = K$

ΔG^0	K
$\Delta G^0 = 0$	K = 1
$\Delta G^0 < 0$	K > 1
$\Delta G^0 > 0$	K < 1

Free Energy and Equilibrium

$$\Delta G = \Delta G^\circ + RTLn(Q)$$

So if at equilibrium $\Delta G = 0$ and $K = Q$ …

$$0 = \Delta G^\circ + RTLn(K)$$

Then rearrange…

$$\Delta G^\circ = -RTLn(K)$$

where R=8.314J/mol•K

Reminder….

If you use the Hess's Law style method for Gibbs problems, where you have to add together various rxns, you need to edit your Keq value when you add/multiply your equations!

Multiplying an Equation – Raise K to that exponent

Double the Rxn = K^2 Half the Rxn = $K^{½}$

Adding Reactions at the End – Multiply K values

$K_{overall} = K_1 \times K_2 \times K_3$, etc

Then you can do things like - $\Delta G^\circ = -RTLn(K)$

Free Energy and Equilibrium

So if…

$$\Delta \mathbf{G}^{\circ} = \mathbf{-RTLn(K)}$$

And if…

$$\Delta \mathbf{G}^{\circ} = \Delta \mathbf{H}^{\circ} - \mathbf{T}\Delta \mathbf{S}^{\circ}$$

Then…

$$\Delta G^{0} = -RT \ln(K) = \Delta H^{0} - T\Delta S^{0}$$

Free Energy and Equilibrium

$$\Delta G^0 = -RT \ln(K) = \Delta H^0 - T\Delta S^0$$

Rearrange to solve for ln(K)….

$$\ln(K) = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} = -\frac{\Delta H^0}{R}\left(\frac{1}{T}\right) + \frac{\Delta S^0}{R}$$

So…. ln(K) $\propto$ 1/T

And that equation looks like y = mx + b ….

Free Energy and Equilibrium

You can find ∆H° and ∆S° by graphing!

$$\ln(K) = -\frac{\Delta H°}{R}\left(\frac{1}{T}\right) + \frac{\Delta S°}{R}$$

y = m   x   + b

1st - Graph ln(K) vs $\left(\frac{1}{T}\right)$

2nd - Find line of best fit (Excel or graphing calculator)

3rd - Slope $= -\frac{\Delta H°}{R}$ Intercept $= \frac{\Delta S°}{R}$

Soooo many rearrangements…

- There are so many ways to rearrange, substitute, and solve for various things when it comes to Thermodynamics.

    You HAVE to have decent algebra skills!

- My best advice if algebra is not your strong suit…
    - Practice over and over until it becomes "muscle memory" how to rearrange.
    - Every time you have a question that requires a different equation rearrangement/substitution, write it down! Start making your own equation cheat sheet.

For the Rx: **2NO(g) + O$_2$(g) → 2NO$_2$(g)** ΔS°_{rxn}= -146.5 J/mol•K
Calculate the standard molar entropy of O$_2$(g).
$\Delta S^\circ_{NO(g)}$ = 210.8 J/mol•K , $\Delta S^\circ_{NO2(g)}$ = 240.1 J/mol•K

A -175.8 J mol^{-1}K^{-1}

B 269.4 J mol^{-1}K^{-1}

C -205.1 J mol^{-1} K^{-1}

D 205.1 J mol^{-1} K^{-1}

E None of the above

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$$\Delta S_{rxn} = \Sigma \Delta S_{Products} - \Sigma \Delta S_{reactants}$$

A -175.8 J mol^{-1}K^{-1}

$(-146.5) = [\ 2(240.1)\ ] - [\ 2(210.8) + \Delta S^\circ_{O2}\ ]$

B 269.4 J mol^{-1}K^{-1}

ΔS°_{O2} = 205.1 Jmol^{-1}K^{-1}

C -205.1 J mol^{-1} K^{-1}

D **205.1 J mol^{-1} K^{-1}**

E None of the above

For the following Rx: **$N_2(g) + H_2(g) \rightarrow NH_3(g)$**
Calculate the standard Free Energy, $\Delta G°$ for the rxn at 25°C.
$\Delta H° = -264kJ/mol$ **$\Delta S° = -278$ J/mol•K**

(A) -82.5 KJ mol^{-1}

(B) -181 KJ mol^{-1}

(C) -6686 KJ mol^{-1}

(D) 181 KJ mol^{-1}

(E) None of the above

For the following Rx: $N_2(g) + H_2(g) \rightarrow NH_3(g)$
Calculate the standard Free Energy, $\Delta G°$ for the rxn at 25°C.
$\Delta H° = -264kJ/mol$ $\Delta S° = -278 \text{ J/mol} \bullet K$

A -82.5 KJ mol^{-1}

B **-181** **KJ mol^{-1}**

C -6686 KJ mol^{-1}

D 181 KJ mol^{-1}

E None of the above

$\Delta G° = \Delta H° - T\Delta S°$

$\Delta G° = (-264) - 298(-0.278)$

$\Delta G° = -181 \text{ KJ mol}^{-1}$

Careful about units matching!
H and S usually don't match!
Convert before you use them!

Calculate the Boiling Point of BCl_3.

$BCl_{3(l)} \leftrightarrow BCl_{3(g)}$. Given:

	$\Delta H°_f$ kJ/mol	$S°$ J/mol k
BCl_3 (*l*)	-418	209
BCl_3 (g)	-395	290

(A) 352 K

(B) 275 K

(C) 322 K

(D) 284 K

(E) 10 K

Calculate the Boiling Point of BCl_3.

$BCl_{3(l)} \leftrightarrow BCl_{3(g).}$ Given:

Phase change - at equilibrium!
So $\Delta G = 0$

	$\Delta H°_f$ kJ/mol	$\Delta S°$ J/mol k
BCl_3 (*l*)	-418	209
BCl_3 (g)	-395	290

A 352 K

B 275 K $\Delta G° = \Delta H° - T\Delta S°$

C 322 K $0 = (-395 – -418) – T(0.290 – 0.209)$

D **284 K**   T = 284 K

E 10 K

What is $\Delta G°$ for the following Rx @ 25.0°C:

2 NH$_3$(g) $\rightarrow$ N$_2$(g) + 3 H$_2$(g) $\Delta H°= 92.4$ kJ, $\Delta S°= 198$ J/K

A -58911.6 kJ

B 33.40 kJ   **ΔG° = ΔH° - TΔS°**

C -497.64 kJ $\Delta G° = (92.4) – 298(0.198)$

D 87.45 kJ $\Delta G° = 33.4$ kJ

E -4857.6 kJ

What is $\Delta G°$ for the following Rx @ 25.0°C:
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Under standard conditions (1 atm of NH_3, N_2 and H_2) and at 298 K, what will be formed? ($\triangle G° = 33.4$ kJ)

2 NH_3(g) → N_2(g) + 3 H_2(g)

A NH_3

B N_2 and H_2

C   Equal amounts of all three gases

D   Need more information

Under standard conditions (1 atm of NH_3, N_2 and H_2) and at 298 K, what will be formed? ($\triangle G° = 33.4$ kJ)

2 NH_3(g) → N_2(g) + 3 H_2(g)

$\triangle$G = + so not spontaneous in reverse direction, reactants will be produced not products

A **NH_3**

B N_2 and H_2

C Equal amounts of all three gases

D Need more information

Calculate the equilibrium constant for this reaction at 298 K.
2 NH$_3$(g) → N$_2$(g) + 3 H$_2$(g) ($\triangle$G° = 33.4 kJ)

A 1.014

B 609048.5

C 1.397 E-6

D Need to know equilibrium [ ]'s to calculate Keq

Calculate the equilibrium constant for this reaction at 298 K.

$2 NH_3(g) \rightarrow N_2(g) + 3 H_2(g)$ ($\triangle G° = 33.4$ kJ)

$$\triangle G° = -RT \ln(K)$$

A 1.014 $33400 = -(8.314)(298)\ln(K)$

B 609048.5 $-13.48 = \ln(K)$

C **1.397 E-6** $e^x = y$ $\ln(y) = x$ $e^{-13.48} = K$

D Need to know $K = 1.397 \times 10^{-6}$
equilibrium [ ]'s
to calculate Keq