N7 - THERMODYNAMICS

Gibbs Free Energy

Link to YouTube Presentation: https://youtu.be/9IUI6T5ynfU

N7 - THERMODYNAMICS

Gibbs Free Energy

Target: I can use the relationships between Gibbs Free Energy, Enthalpy, Entropy, and Equilibrium to solve for a variety of things.

PART 1

HOW WE GOT THE GIBBS EQUATION AND MENTAL MATH USING IT

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

We saw last time that:

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

This turns into…

Gibbs Free Energy

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

This should remind you of something!!!

Gibbs Free Energy

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

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

Therefore...

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

Another helpful rearrangement!

Gibbs Free Energy

$$\Delta G_{\mathrm{sys}} = -T\Delta S_{\mathrm{univ}}$$

- Because ΔS_{univ} determines if a process is spontaneous, ΔG also determines spontaneity.
- ΔS_{univ} is positive when spontaneous, **so ΔG is negative when spontaneous**

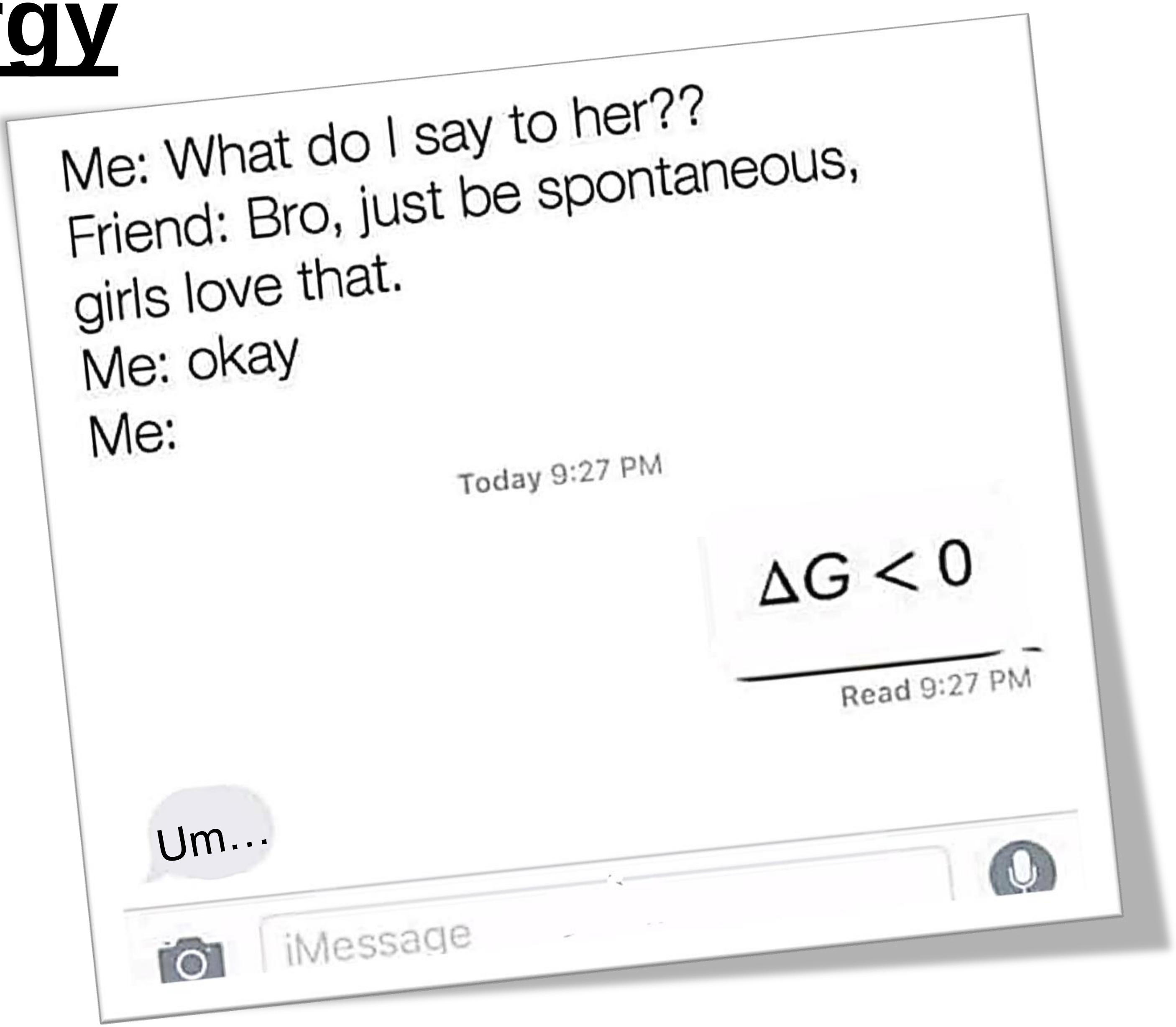
Gibbs-Helmholtz Equation

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

Important Equation!!!

Gibbs Free Energy

A process will be spontaneous when ΔG is negative



Me: What do I say to her??
Friend: Bro, just be spontaneous, girls love that.
Me: okay
Me:

Today 9:27 PM

$\Delta G < 0$

Read 9:27 PM

Um…

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

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

Mental Math with Gibbs Free Energy

BEST COMBO!

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

ΔH	ΔS	ΔG	At…

Remember T is in Kelvin, always a positive number

Mental Math with Gibbs Free Energy

BEST COMBO!

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

ΔH	ΔS	ΔG	At…
− ***exothermic***	+ ***more disorder***	− ***ALWAYS spont.***	Any temperature

$$(\text{Negative \#}) - {}_{\text{any}}T(\text{Positive \#}) = \text{Always Negative \#}$$

Remember T is in Kelvin, always a positive number

Mental Math with Gibbs Free Energy

WORST COMBO!

<table>
<tr><td colspan="4">$\Delta H_{sys} - T\Delta S_{sys} = \Delta G_{sys}$</td></tr>
<tr><td>ΔH</td><td>ΔS</td><td>ΔG</td><td>At…</td></tr>
<tr><td></td><td></td><td></td><td></td></tr>
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Mental Math with Gibbs Free Energy

WORST COMBO!

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

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

VARIABLE COMBO!

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

ΔH	ΔS	ΔG	At…

Mental Math with Gibbs Free Energy

VARIABLE COMBO!

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

ΔH	ΔS	ΔG	At…
+ ***endothermic***	**+** ***more disorder***	**−** ***spont.***	**High Temp**

(Positive #) – $_{\text{large}}$T(Positive #) = Negative #

ΔH needs to be a smaller positive number than $T\Delta S_{sys}$

Small # - Big # = Negative #

$$\Delta H < T\Delta S_{sys}$$

Mental Math with Gibbs Free Energy

VARIABLE COMBO!

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

ΔH	ΔS	ΔG	At…

Mental Math with Gibbs Free Energy

VARIABLE COMBO!

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

ΔH	ΔS	ΔG	At…
– *exothermic*	– *less disorder*	– *spont.*	Low Temp

(Negative #) – $_{small}$T(Negative #) = Negative #

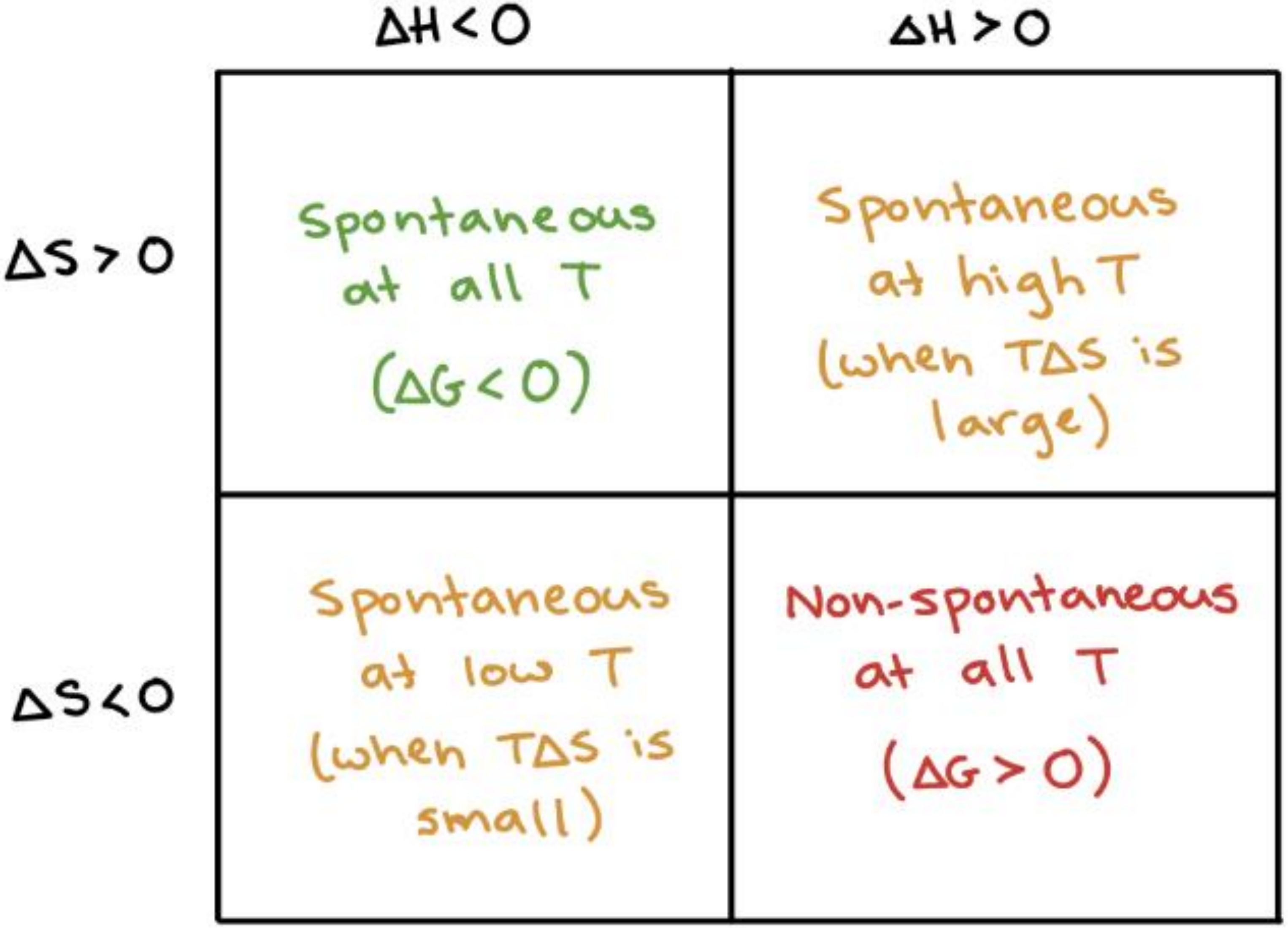
Notice the double negative! → (Negative #) + (Positive #)

ΔH needs to be a larger negative than $T\Delta S_{sys}$

$\Delta H < T\Delta S_{sys}$

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

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! ☺

Now it is time for some math!

Yay!

Calculating Free Energy

Method #1- Standard Free Energy of Formations

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

$\Delta G_f°$ of an element in its standard state is zero

Calculating Free Energy

Method #2- **Gibbs-Helmohotz Equation**

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

For reactions at a constant temperature

Calculating Free Energy

Method #3- A variation of Hess's Law

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

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

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

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

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

PART 2

CONNECTION TO EQUILIBRIUM

Free Energy and Equilibrium

The value of $\Delta G°$ can indicate the ratios of products to reactants at equilibrium.

The ratio of products to reactants is also indicated by a value you already know from equilibrium....

K

“Rat Link Equation”

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

where R=8.314J/mol•K

CAREFUL!!!

Δ G° in kJ but.... R in J

CONVERT UNITS TO MATCH!

Solving for K

$$\mathrm{Ln}(K) = \frac{-\Delta G^{\circ}}{RT}$$

Isolate Ln(K).

Do you remember how to "undo" a natural logarithm???

CAREFUL!!!

$\Delta G°$ in kJ but.... R in J

CONVERT UNITS TO MATCH!

Solving for K

Make sure it is an EXPONENT!

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

e raised to all that other "stuff" gives you what is inside the natural logarithm!

CAREFUL!!!

Δ G° in kJ but.... R in J
CONVERT UNITS TO MATCH!

Careful!

Not always at standard state!

In that case you would use **ΔG** instead of $\Delta G°$

Like using Q instead of K if you weren’t at equilibrium!

Gibbs at Equilibrium

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

$\Delta G = 0$ → @ equilibrium!
BUT $\Delta G°$ does NOT always = 0 at equilibrium!

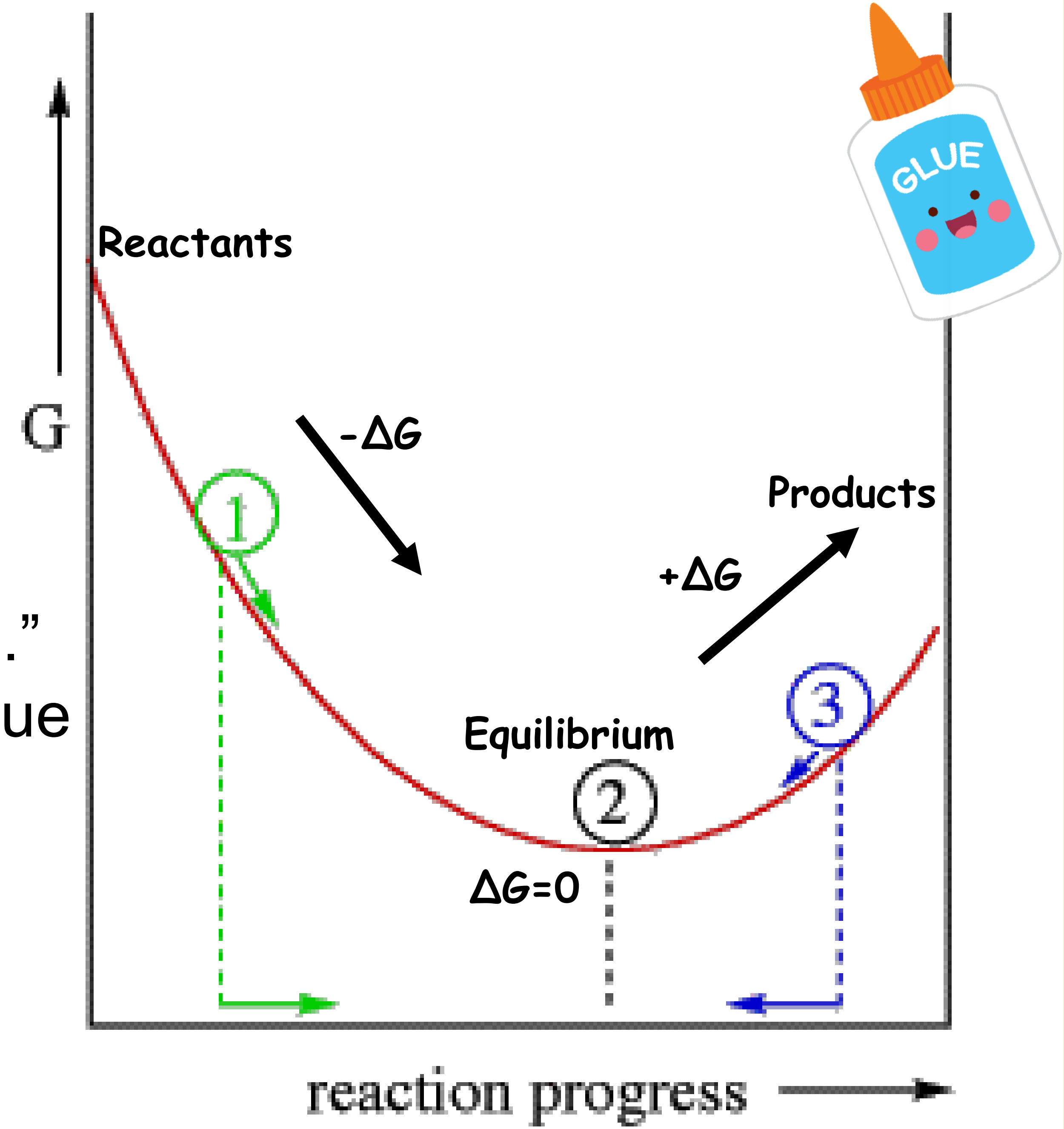
$\Delta G° = 0$ ***only if*** [reactants] = [products] when at equilibrium.

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

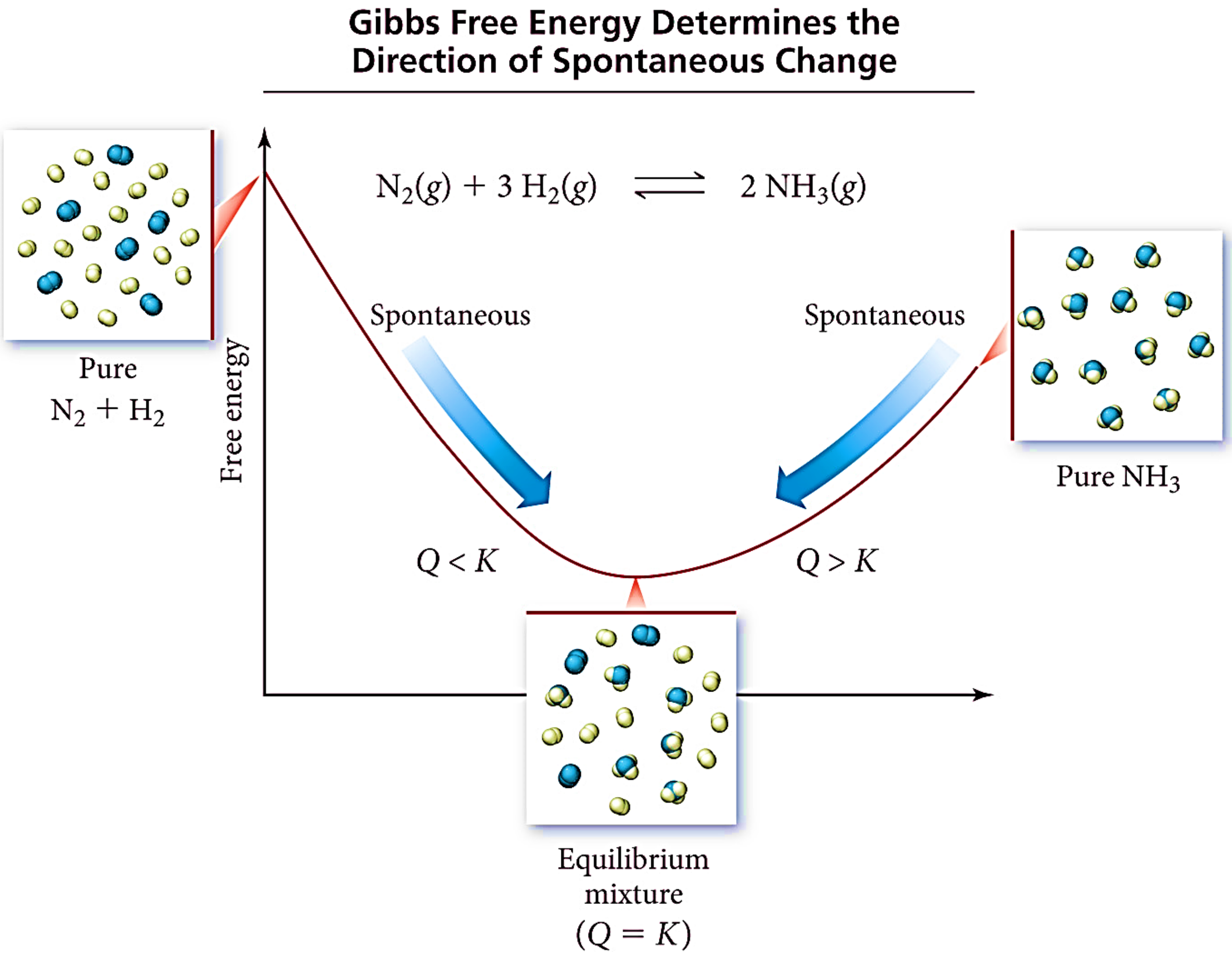
1 G decreasing, forward direction
“thermodynamically favorable,”
spontaneous, will proceed.

3 G increasing, forward direction
NOT “thermodynamically favorable.”
Non-spontaneous, rxn won’t continue
forward on its own.

2 ΔG, at equilibrium.
No net change in rxn.



Gibbs at Equilibrium



Gibbs Free Energy Determines the Direction of Spontaneous Change

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 $K = Q$

ΔG	**K vs Q**	
$\Delta G = 0$	$K = Q$	@ equilibrium
$\Delta G < 0$	$K > Q$	Shift right
$\Delta G > 0$	$K < Q$	Shift left

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

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

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

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

Then rearrange…look what we are back to! ☺

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

where $R = 8.314 J/mol \bullet K$

Free Energy and Equilibrium

So if…

$$\Delta G^\circ = -RT\mathrm{Ln}(K)$$

And if…

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

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 ΔH° and ΔS° by graphing!

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

$$y \quad = \quad m \quad x \quad + \quad b$$

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.

A Few Odds and Ends Reminders

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

Reversing a reaction – take reciprocal of K value

$K' = 1/K$

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

Free Energy and Pressure

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

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

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

Phase Changes

- **Phase changes are equilibriums!**
- **So during a phase change $\Delta G = 0$**
  - **Helps you do calculations to figure out the temperature at which phase changes can happen!**

Technically...

We shouldn't be using $\Delta G = 0$ with $\Delta H°$ and $\Delta S°$ values, since $\Delta H°$ and $\Delta S°$ would usually be at the "standard" 25°C...but we just pretend they are not temperature dependent to be able to approximate our answer. Is that "bad" ??? Sure...but do we care??? Apparently not! ☺

Some Practice Problems

#1 - For the following Rx: **$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$**

Calculate the standard Free Energy, ΔG° for the rxn at 25°C.

ΔH°= -264kJ/mol   ΔS°= -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

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ΔH°= -264kJ/mol **ΔS°= -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

$\Delta G° = \Delta H° - T\Delta S°$

$\Delta G° = (-264) - 298(-0.278)$

$\Delta G° = -181$ KJ mol^{-1}

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

#2 - Calculate the Boiling Point of BCl_3.

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

	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

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

- A 352 K
- B 275 K
- C 322 K
- D **284 K**
- E 10 K

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

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

$T = 284$ K

#3 - Under standard conditions (1 atm of NH_3, N_2 and H_2) and at 298 K, what substance(s) will be formed? (ΔG° = 33.4 kJ)

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

- A NH_3
- B N_2 and H_2
- C Equal amounts of all three gases
- D Need more information

#3 - Under standard conditions (1 atm of NH_3, N_2 and H_2) and at 298 K, which substance(s) will be formed? ($\Delta G° = 33.4$ kJ)

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

$\Delta G = +$ so not spontaneous in forward 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

#4 - Calculate the equilibrium constant for this reaction at 298 K.
$2\ NH_3(g) \rightarrow N_2(g) + 3\ H_2(g)$ ($\Delta G°$ = 33.4 kJ)

A 1.014

B 609048.5

C 1.397 E-6

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

#4 - Calculate the equilibrium constant for this reaction at 298 K.

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

$\Delta G° = -RT\ \ln(K)$

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

$-13.48 = \ln(K)$

$\ln(y) = x \qquad e^{x} = y$

$e^{-13.48} = K$

$K = 1.397 \times 10^{-6}$

- Ⓐ 1.014
- Ⓑ 609048.5
- Ⓒ **1.397 E-6**
- Ⓓ Need to know equilibrium [ ]'s to calculate Keq

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