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:

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

This turns into…

Gibbs Free Energy

It can be shown that:

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

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

BEST COMBO!

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

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

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…
+ *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…**
– *exothermic*	**–** *less disorder*	**–** *spont.*	Low Temp

$$(\text{Negative \#}) - {}_{\text{small}}T(\text{Negative \#}) = \text{Negative \#}$$

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

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

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

Mental Math with Gibbs Free Energy

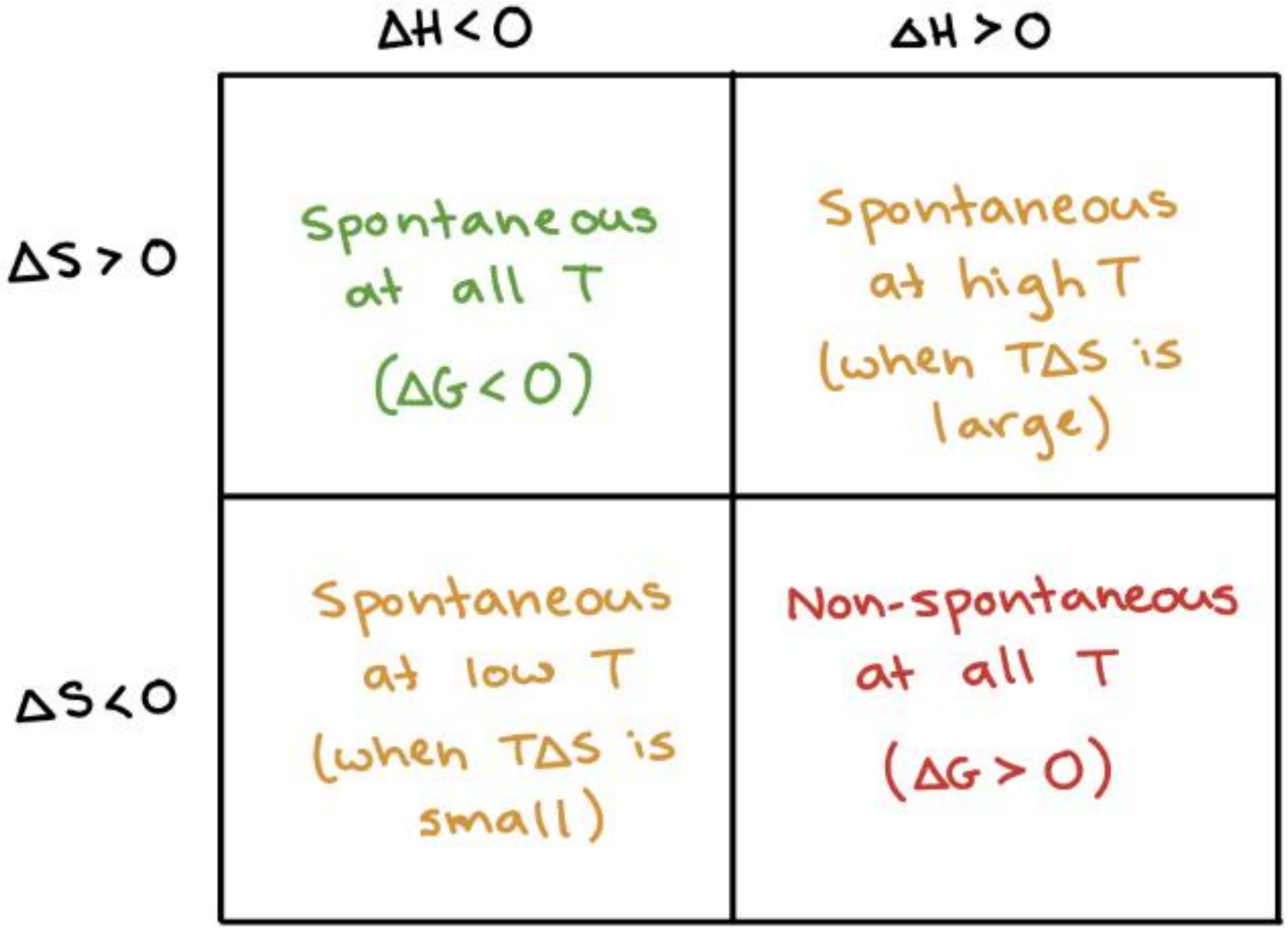
This always makes my brain feel scrambled… figure out what works for you.

- 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 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 ($\Delta G > 0$)

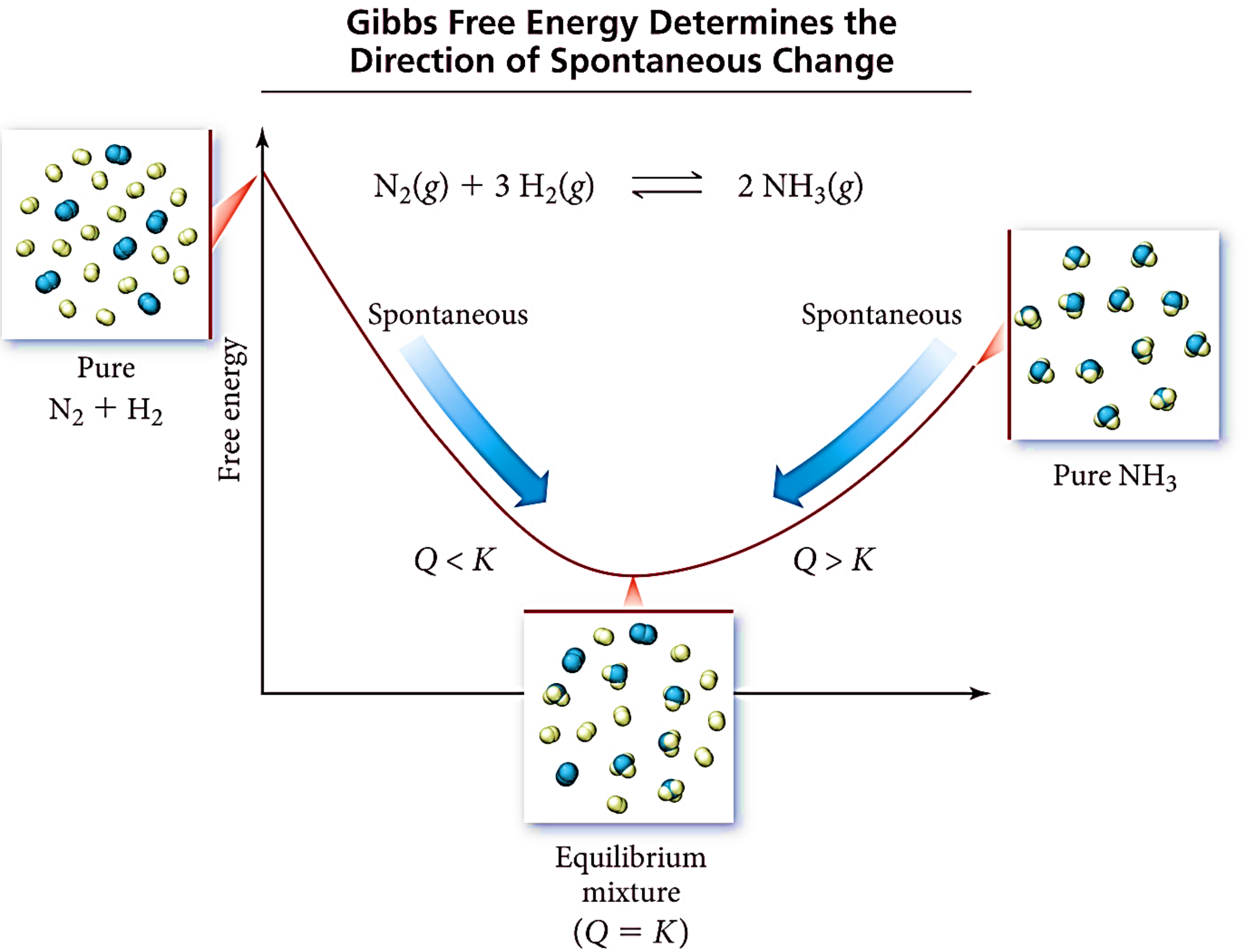
So many versions online, find one you like! If you find a good one, always share with me! ☺

Gibbs at Equilibrium

When $\Delta G = 0$

the reaction is at **equilibrium**.

Gibbs at Equilibrium



Calculating Free Energy

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

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

For reactions at a constant temperature

Calculating Free Energy

Method #2- A variation of Hess's Law

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

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

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

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

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

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

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

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

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 $R=8.314 J/mol \bullet K$

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

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

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

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…

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

Free Energy and Equilibrium

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

Rearrange to solve for ln(K)….

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

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!

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

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: **$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$** $\Delta S°_{rxn}$= -146.5 J/mol•K
Calculate the standard molar entropy of $O_2(g)$.
$\Delta S°_{NO(g)}$ = 210.8 J/mol•K , $\Delta S°_{NO2(g)}$ = 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

For the Rx: **$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$** $\Delta S°_{rxn}$= -146.5 J/mol•K
Calculate the standard molar entropy of $O_2(g)$.
$\Delta S°_{NO(g)}$ = 210.8 J/mol•K , $\Delta S°_{NO2(g)}$ = 240.1 J/mol•K

$$\Delta \boldsymbol{S}_{\boldsymbol{rxn}} = \Sigma\, \Delta \boldsymbol{S}_{\boldsymbol{Products}} - \Sigma\, \Delta \boldsymbol{S}_{\boldsymbol{reactants}}$$

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

$(-146.5) = [\ 2(240.1)\ ] – [\ 2(210.8) + \Delta S°_{O2}\ ]$

$\Delta S°_{O2}$ = 205.1 $Jmol^{-1}K^{-1}$

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, 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

ΔG° = ΔH° - TΔS°

ΔG° = (-264) – 298(-0.278)

ΔG° = -181 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:

	ΔH°_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:

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

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

A 352 K

B 275 K

C 322 K

D **284 K**

E 10 K

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

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

$$T = 284\ K$$

What is ΔG° for the following Rx @ 25.0°C:

$2\ NH_3(g) \rightarrow N_2(g) + 3\ H_2(g)$ ΔH°= 92.4 kJ, ΔS°= 198 J/K

- A -58911.6 kJ
- B 33.40 kJ
- C -497.64 kJ
- D 87.45 kJ
- E -4857.6 kJ

ΔG° = ΔH° - TΔS°

ΔG° = (92.4) – 298(0.198)

ΔG° = 33.4 kJ

What is ΔG° for the following Rx @ 25.0°C:

$2\ NH_3(g) \rightarrow N_2(g) + 3\ H_2(g)$ ΔH°= 92.4 kJ, ΔS°= 198 J/K

- A -58911.6 kJ
- B **33.40 kJ**
- C -497.64 kJ
- D 87.45 kJ
- E -4857.6 kJ

ΔG° = ΔH° - TΔS°

ΔG° = (92.4) – 298(0.198)

ΔG° = 33.4 kJ

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

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

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

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

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

Calculate the equilibrium constant for this reaction at 298 K.

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

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

$\Delta G° = -RT\ \ln(K)$

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

$-13.48 = \ln(K)$

$e^x = y$ $\ln(y) = x$

$e^{-13.48} = K$

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