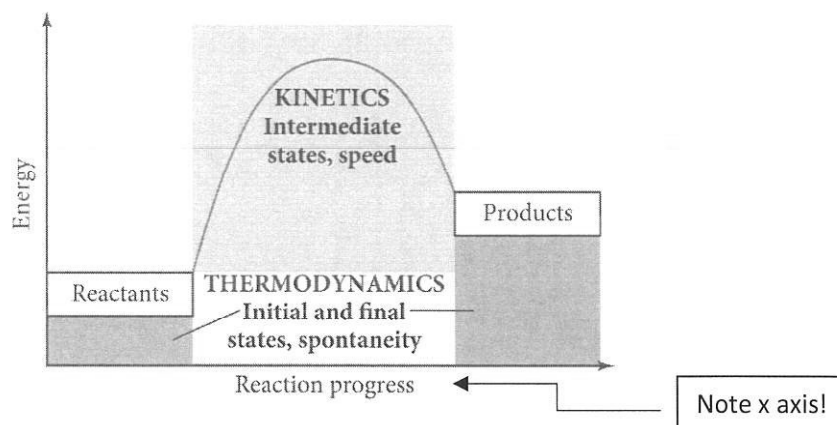A Brief Interlude:

Thermodynamics (will a reaction happen spontaneously?) **vs Kinetics** (how fast will this reaction happen?)

Note x axis!

---

and now back to... Thermodynamically Favorable Processes

Thermodynamically favored (aka spontaneous) processes take place **without *net* input** of energy from external sources.

Neither entropy (ΔS) nor enthalpy (ΔH) alone can tell us if a reaction is spontaneous:

→ must use a combination of the two: _Gibb's_ **Free Energy!**

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$ on F.C. ☺

T = temperature in Kelvin

ΔH = enthalpy change (units of **kJ/mol** or **kJ mol^{-1}**)

ΔS = entropy change (units of **J/(mol K)** or **J mol^{-1} K^{-1}**)

*Notice **difference in units!** You **must** make both units the same (J or kJ) before you calculate ΔG.*

Δ**G** (Gibb's free energy) is the energy associated with a chemical reaction that can be used to do work.

	AP Units (Use on quizzes and tests)		Mastering Chem Units
ΔG	$\dfrac{kJ}{mol_{rxn}}$	or $\dfrac{J}{mol_{rxn}}$	kJ or J
ΔH	$\dfrac{kJ}{mol_{rxn}}$	or $\dfrac{J}{mol_{rxn}}$	kJ or J
ΔS	$\dfrac{J}{mol \cdot K}$		$\dfrac{J}{K}$

The sign of ΔG tells if any given process is thermodynamically favored:

❖ $-\Delta G$: Thermodynamically favored (spontaneous) ★exergonic

❖ $+\Delta G$: Not thermodynamically favored (non-spontaneous) ★endergonic

❖ $\Delta G = 0$: At equilibrium

reaction quotient (Q_c)
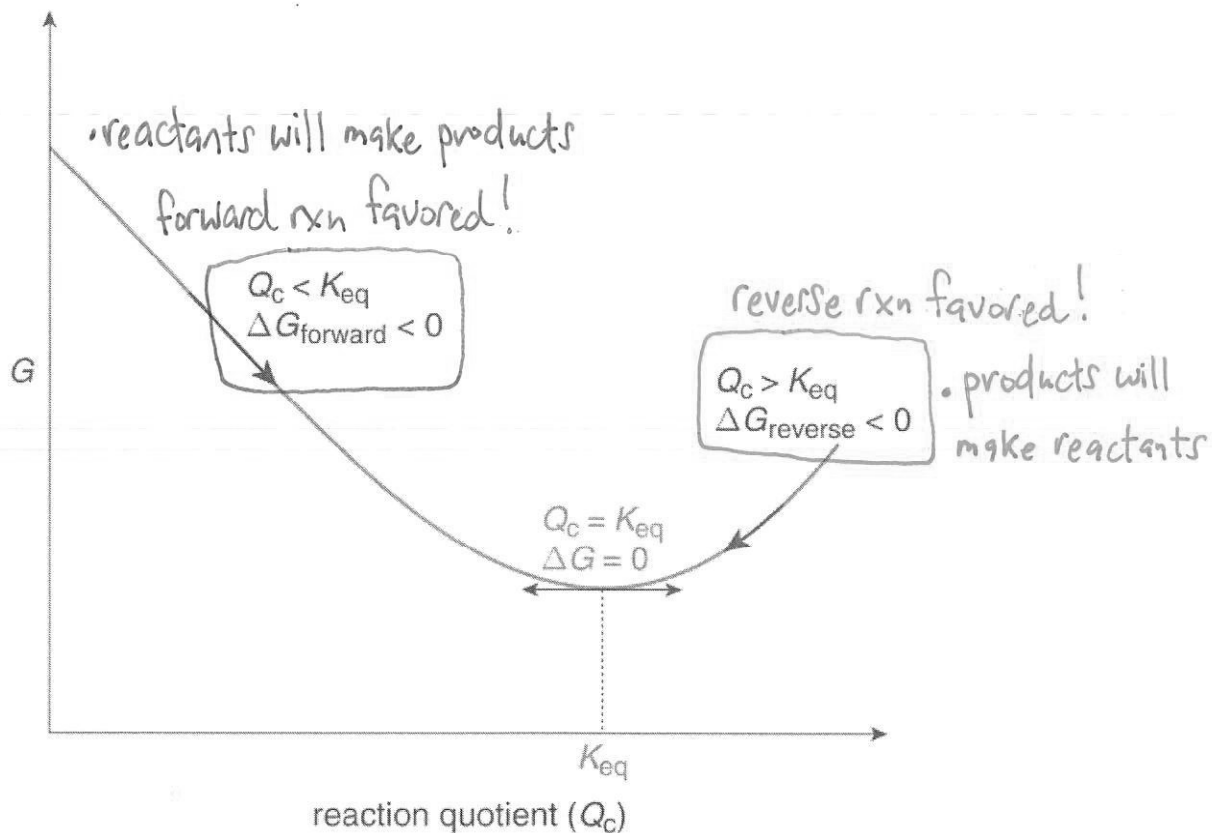
You can also calculate the standard Gibb's Free Energy Change for a reaction by comparing the standard free energy of formation of reactants and products: this should look very familiar!

$$\Delta G^0_{reaction} = \sum [G^0_f(products)] - \sum [G^0_f(reactants)]$$ on F.C.

Note: <u>Elements DO have a value of zero for ΔG°</u>, because forming an element from itself results in no change.

Elements ARE zero for: ___ΔH, ΔG___

Elements are NOT zero for: ___ΔS___

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

What does it mean when a reaction is "driven" by enthalpy, entropy, or both?

Nature favors:

1. $+\Delta S$ (increasing entropy, greater disorder)
2. $-\Delta H$ (exothermic, release of energy)

For a reaction to be thermodynamically favorable, ΔG must be negative, but that doesn't mean you need increasing entropy AND an exothermic process for a reaction to proceed spontaneously!

- **Driven by enthalpy:** a very exothermic reaction ($-\Delta H$) overcomes a decrease in entropy

  Example: The formation of NaCl(s) from its elements is spontaneous and releases lots of heat.

  $$2\,Na(s) + Cl_2(g) \rightarrow 2\,NaCl(s)$$
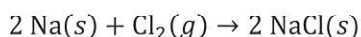
  This process clearly involves a decrease in entropy (–ΔS), since a gas molecule becomes a solid. However, it is a highly exothermic reaction (–ΔH). Because the large –ΔH is more negative than the positive –TΔS term, overall ΔG is negative, and the reaction is thermodynamically favored.
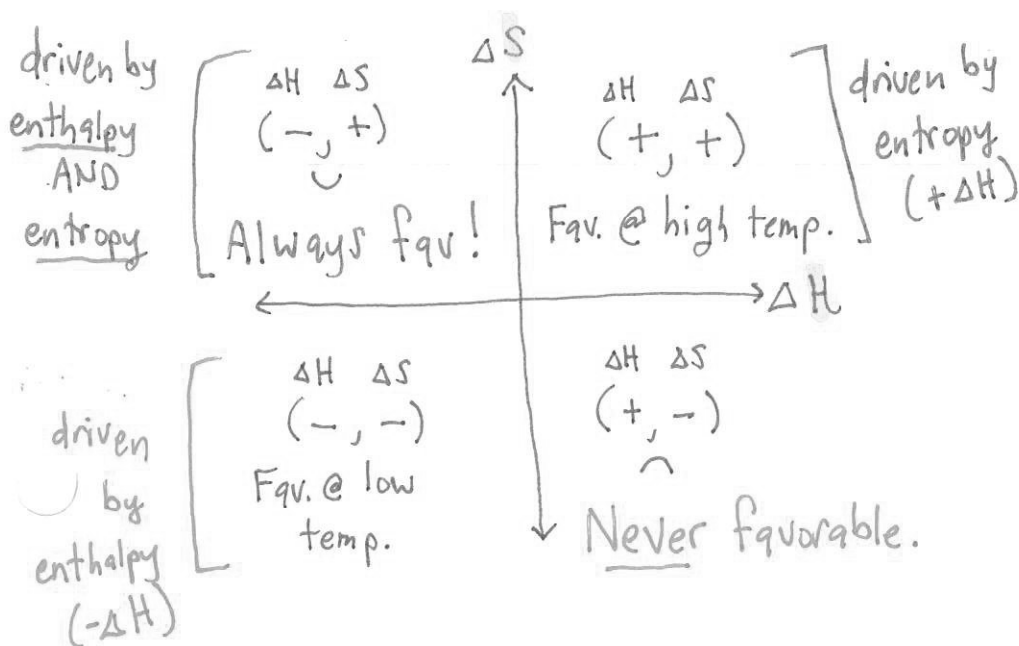
- **Driven by entropy:** an endothermic reaction occurs spontaneously because of a highly $+\Delta S$ ΔS

  Example: NaNO₃(s) dissolves in water with a noticeable decrease in temperature.

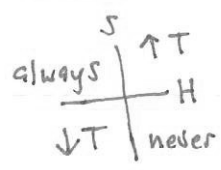 $$NaNO_3(s) \rightarrow Na^+(aq) + NO_3^-(aq)$$
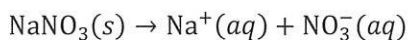
  This is an endothermic reaction, so ΔH is positive. However, NaNO₃ does dissolve, so ΔG must be negative. This means that ΔS must be very positive, so that the negative –TΔS term is sufficiently negative to overcome the positive ΔH, and the reaction is thermodynamically favored.

You can use the signs of ΔS and ΔH (together with the reaction ΔG = ΔH – TΔS) to predict qualitatively the spontaneity of a given reaction. You can show this graphically, which leads to the best graph of all time (but SHHHH! It's a secret. ☺)

driven by enthalpy AND entropy

ΔH ΔS
$(-, +)$
Always fav!

ΔS

ΔH ΔS
$(+, +)$
Fav. @ high temp.

driven by entropy
$(+\Delta H)$

→ ΔH

driven by enthalpy
$(-\Delta H)$

ΔH ΔS
$(-, -)$
Fav. @ low temp.

ΔH ΔS
$(+, -)$
Never favorable.

Short version:

	S
always	↑T
	H
↓T	never

You can also consider this in a table:

ΔH	ΔS	-TΔS	ΔG	The reaction is thermodynamically:
−	+	−	−	favored at all temperatures
+	−	+	+	not favored at all temperatures
−	−	+	+/−	favored only at low temperatures
+	+	−	+/−	favored only at high temperatures

Is it possible to have a reaction with –ΔG that doesn't happen?

Yes! Well, kind of. It is possible for a technically spontaneous reaction (i.e. –ΔG) to occur so ___slowly___ that no measurable products form. This happens if a reaction has a VERY high ___activation___ energy – we'll talk more about this during our next unit! When this happens, the reaction is said to be under ___Kinetic___ control.

How can you "force" a reaction to run if it has +ΔG?

There are actually multiple ways! We already know about one of them.

1. Apply an external ___Source___ of energy, such as electricity in electrolysis reactions or light in photosynthesis.

2. ___Couple___ thermodynamically unfavored reactions with thermodynamically favored ones, via their common intermediates.

$$glucose + fructose \rightleftharpoons sucrose \qquad \Delta G = +27\ kJ/mol$$
$$ATP + H_2O \rightleftharpoons ADP + P_i \qquad \Delta G = -30\ kJ/mol$$
$$\overline{glucose + fructose + ATP \rightleftharpoons sucrose + ADP + P_i \qquad \Delta G = -3 kJ/mol}$$

Let's Practice!

1. Given the values for ΔH, ΔS, and T, determine whether each of the following sets of data represent thermodynamically favorable or non-thermodynamically favorable processes.

	ΔH (kJ/mol)	ΔS (J/mol K)	T (K)	
a.	40	300	130	$\Delta G = 40\frac{kJ}{mol} - (130K)(0.300\frac{kJ}{mol \cdot K}) = 1\ kJ/mol\ (+\Delta G)$
b.	40	300	150	$\Delta G = 40\frac{kJ}{mol} - (150K)(0.300\frac{kJ}{mol \cdot K}) = -5\ kJ\ (-\Delta G)$
c.	40	−300	150	$+\Delta H, -\Delta S \Rightarrow$ never favorable
d.	−40	−300	130	$\Delta G = (-40\frac{kJ}{mol}) - (130K)(-0.300\frac{kJ}{mol K}) = -1\frac{kJ}{mol}\ (-\Delta G)$
e.	−40	300	150	$-\Delta H, +\Delta S \Rightarrow$ always favorable

not a.

fav! b.

not c.

fav! d.

fav! e.

2. Using data for ΔH° and S°, calculate ΔG° for the following reaction at 25°C and 1 atm.

$$Cr_2O_3(s) + 2\ Al(s) \rightarrow Al_2O_3(s) + 2\ Cr(s)$$
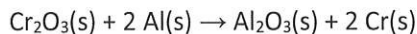
Substance	ΔH°f(kJ/mol)
$Cr_2O_3(s)$	-1128 kJ/mol
$Al_2O_3(s)$	-1676 kJ/mol

Substance	S°(J/mol K)
Cr (s)	24 J/mol K
Al (s)	28 J/mol K
$Al_2O_3(s)$	51 J/mol K
$Cr_2O_3(s)$	81 J/mol K

$$\Delta H^\circ_{rxn} = \Sigma \Delta H^\circ_f (pr) - \Sigma \Delta H_f^\circ (re)$$

$$= [Al_2O_3 + 2Cr] - [Cr_2O_3 + 2Al]$$

$$= [-1676 + \emptyset] - [-1128 + \emptyset]$$

$$= -548\ kJ/mol$$

$$\Delta S^\circ_{rxn} = \Sigma S^\circ(pr) - \Sigma S^\circ(re)$$

$$= [Al_2O_3 + 2Cr] - [Cr_2O_3 + 2Al]$$

$$= [51 + 2(24)] - [81 + 2(28)]$$

$$= -38\ J/mol \cdot K \quad \text{Convert!}$$

$$\Delta G^\circ_{rxn} = \Delta H^\circ - T\Delta S^\circ = -548 \frac{kJ}{mol} - (298\ K)(-0.038\ kJ/mol \cdot K) = \boxed{-537 \frac{kJ}{mol\ rxn}}$$

3. Given the values of ΔG° you calculated in #2, calculate the equilibrium constant, K, for the following reaction (at 25°C):

$$Cr_2O_3(s) + 2Al(s) \rightarrow Al_2O_3(s) + 2Cr(s)$$
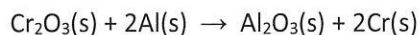
Is this reaction thermodynamically favorable? Use your calculated Gibb's free energy and equilibrium constant to justify your answer.

$$\Delta G^\circ = -RT \ln K \Rightarrow \ln K = \frac{-\Delta G^\circ}{RT} \quad \left] \begin{array}{l} \text{Need } \Delta G^\circ \text{ in } J/mol \\ \left(b/c\ R = \frac{J}{mol \cdot K}\right) \end{array} \right.$$

$$\ln K = \frac{5.37\ E\ 5\ J/mol}{(8.314 \frac{J}{mol \cdot K})(298\ K)} = 216.\underline{74}$$

3 s.f. (don't round til end!)

$$\Rightarrow K = e^{216.\underline{74}} = \boxed{1.35 \times 10^{94}} \quad K \gg 1$$

→ This rxn is very thermodynamically favorable! -ΔG and K >1 both indicate a thermodynamically fav. reaction.

Multiple Choice Practice FTW!

Use the following information to answer questions 4 – 6.

Reaction 1: $N_2H_4(l) + H_2(g) \rightarrow 2NH_3(g)$ $\Delta H = ?$

Reaction 2: $N_2H_4(l) + CH_4O(l) \rightarrow CH_2O(g) + N_2(g) + 3H_2(g)$ $\Delta H = -37 \text{ kJ/mol}_{rxn}$

Reaction 3: $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ $\Delta H = -46 \text{ kJ/mol}_{rxn}$

Reaction 4: $CH_4O(l) \rightarrow CH_2O(g) + H_2(g)$ $\Delta H = -65 \text{ kJ./mol}_{rxn}$
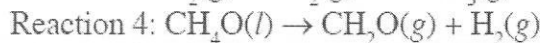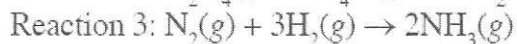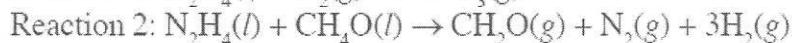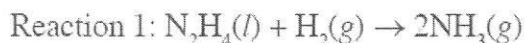
4. What is the enthalpy change for reaction 1? *Use rxns 2-4 : Hess's Law!*

   a. $-148 \text{ kJ/mol}_{rxn}$ b. -56 kJ/mol_{rxn} (c.) -18 kJ/mol_{rxn} d. $+148 \text{ kJ/mol}_{rxn}$

   (Rxn 2) ✓
   *(Rxn 3) ✓* $\Delta H_{tot} = -37 - 46 + 65 = -83 + 65 = -18$
   (Rxn 4) flip !

5. If reaction 2 were repeated at a higher temperature, how would the reaction's value for ΔG be affected?

   (a.) It would become more negative because entropy is a driving force behind this reaction. $+\Delta S \Rightarrow$

   b. It would become more positive because enthalpy is a driving force behind this reaction. $\uparrow T \Rightarrow more -\Delta G$

   c. It would become more negative because the gases will be at a higher pressure.

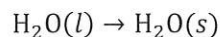   d. It will stay the same; temperature does not affect the value of ΔG.

6. Under what conditions would reaction 3 be thermodynamically favored? $-\Delta H, -\Delta S$

   a. It is always favored.   (c.) It is only favored at low temperatures.

   b. It is never favored.   d. It is only favored at high temperatures.

$$2\,Al(s) + 3\,Cl_2(g) \rightarrow 2\,AlCl_3(s)$$
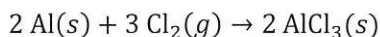
7. The reaction above is not thermodynamically favored under standard conditions, but it becomes thermodynamically favored as the temperature decreases toward absolute zero. Which of the following is true?

   (a.) ΔS and ΔH are both negative.   c. ΔS is negative, and ΔH is positive.

   b. ΔS and ΔH are both positive.   d. ΔS is positive, and ΔH is negative.

$$H_2O(l) \rightarrow H_2O(s)$$

8. Which of the following is true for the above reaction?
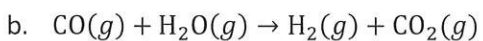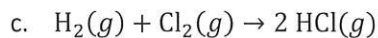
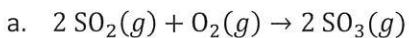   a. The value of ΔS is positive.   c. The value of ΔH is positive.

   (b.) The value of ΔG is positive at 298 K.   d. The reaction is favored at 1.0 atm and 298 K.

9. A chemical reaction has an equilibrium constant, K, equal to 1.0×10^{-6}. If, at a given point in the reaction, the value for the reaction quotient Q is determined to be 2.5×10^{-8}, what is true about Gibb's free energy at that moment?

   a. $\Delta G = 0$ b. $\Delta G > 0$ (c.) $\Delta G < 0$ d. The value of ΔG cannot be determined.

   $K > Q,$ *forward-favored* $= -\Delta G$

10. In which of the following reactions is entropy increasing?

    a. $2 SO_2(g) + O_2(g) \rightarrow 2 SO_3(g)$ c. $H_2(g) + Cl_2(g) \rightarrow 2 HCl(g)$

    b. $CO(g) + H_2O(g) \rightarrow H_2(g) + CO_2(g)$ (d.) $2 NO_2(g) \rightarrow 2 NO(g) + O_2(g)$
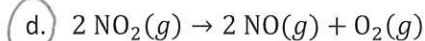
Use the following information to answer questions 11 – 12.

    When calcium chloride ($CaCl_2$) dissolves in water, the temperature of the water increases dramatically. $\Rightarrow -\Delta H$
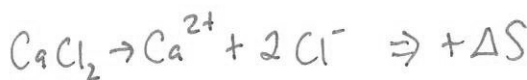
11. During this reaction, energy transfers from:

    a. the reactants to the products.   (c.) the system to the surroundings.

    b. the reactants to the system.   d. the products to the surroundings.

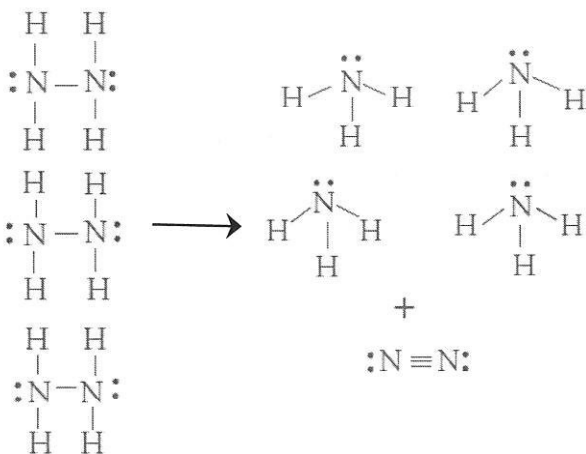12. Which is the primary driving factor behind this reaction? $CaCl_2 \rightarrow Ca^{2+} + 2 Cl^- \Rightarrow +\Delta S$

    a. Entropy   (c.) Both enthalpy and entropy

    b. Enthalpy   d. Neither enthalpy and entropy

13. The reaction shown in the diagram below is accompanied by a large increase in temperature. If all molecules shown are in their gaseous state, which statement accurately describes the reaction?

    (a.) It is an exothermic reaction in which entropy increases.

    b. It is an exothermic reaction in which entropy decreases.

    c. It is an endothermic reaction in which entropy increases.

    d. It is an endothermic reaction in which entropy decreases.

14. When solid ammonium chloride, $NH_4Cl(s)$, is added to water at 25°C, it dissolves and the temperature of the solution decreases. Which of the following is true for the values of ΔH and ΔS for the dissolving process?

$+\Delta H$

	ΔH	ΔS
a.	Positive	Negative
(b.)	Positive	Positive
c.	Negative	Positive
d.	Negative	Negative

$NH_4Cl \rightarrow NH_4^+ + Cl^- \Rightarrow +\Delta S$