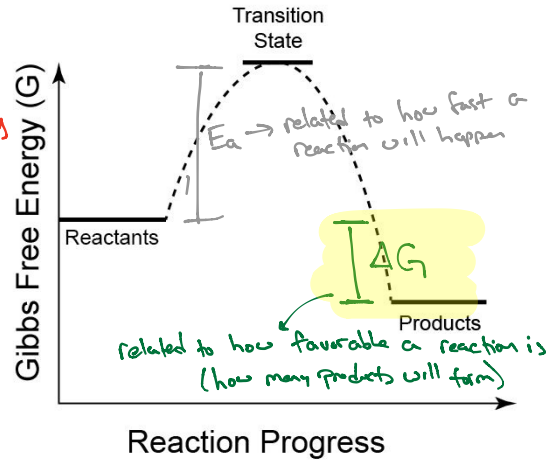When discussing kinetics, we introduced the reaction coordinate image shown here.

The difference is that I'm showing the y-axis with a new label — Gibbs Free energy.

In the next couple of days, we'll learn about the origin of this term, but for now, you should understand that it allows you to figure out IF a reaction is energetically favored.

Transition State

$E_a \rightarrow$ related to how fast a reaction will happen

Reactants

ΔG

Products

related to how favorable a reaction is (how many products will form)

Gibbs Free Energy (G)

Reaction Progress

ΔG is the difference in "free energy (G)" between products and reactants.

- as is always the case, the "Δ" means final - initial, so

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

When $\Delta G < 0$ (negative), a reaction is spontaneous (energetically favorable)
↳ at equilibrium, [Products] > [Reactants]

$\Delta G > 0$ (positive), a reaction is non-spontaneous (unfavorable)

↳ $[Products]_{eq} < [Reactants]_{eq}$

This suggests that there must be a relationship between ΔG & K!

$$\Delta G < 0 \rightarrow K > 1 \quad ([Prod]_{eq} > [React]_{eq})$$

$$\Delta G > 0 \rightarrow K < 1 \quad ([Prod]_{eq} < [React]_{eq})$$

This little symbol means at standard conditions
- $P = 1 \, atm$
- $[\,] = 1M$

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

- So, If K is known, the you can quickly determine the driving force for the reaction

For example:
$K = 100$ @ $298.15K$

$$\Delta G^\circ = -8.314 \frac{J}{mol \cdot K} (298.15K) \ln 100$$

$$\Delta G^\circ = -11,415 \, J/mol \quad \leftarrow spontaneous!$$
- Products are favored!

$K = 0.01$ @ $298.15K$

$\Delta G° = -8.314 \dfrac{J}{mol \cdot K} (298.15K) \ln 0.01$

$\Delta G° = 11,415 \ J/mol \leftarrow$ (+), so non-spontaneous
  − more reactants @ equilibrium

But what happens if concentrations are **not** 1M? So... not @ (standard)

$$\Delta G = \Delta G° + RT \ln Q$$

$\Delta G° = -RT \ln K$

← remember the reaction quotient?
  − calculated exactly the same way as K (but not @ Equilibrium)

When $Q = K$:

$\Delta G = -RT \ln K + RT \ln Q$

$\Delta G = 0$ — the reaction is already at equilibrium. There is not a "driving force" for the forward or reverse reactions.

$K > Q$ ... based on Le Chatelier's Principle, Products are favored

— we predict that $\Delta G < 0$ (spontaneous reaction)

$K = 10$
$Q = 1$
$T = 298.15$

$\Delta G = -8.314 (298.15) \ln 10 + 8.314 (298.15) \ln 1$

$\Delta G = -5,708 \ J/mol$

— yep, Products are favored

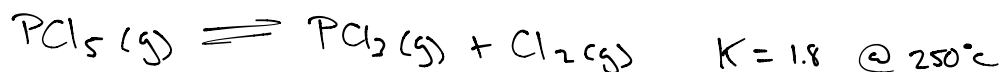$K < Q$ ... Reactants are favored — Predict $\Delta G > 0$

$K = 1$
$Q = 100$
$T = 298.15$

$\Delta G = -8.314 (298.15) \ln 1 + 8.314 (298.15) \ln 100$

$\Delta G = 11,415 \ J/mol$ — non-spontaneous as written !
    (so reactants will form)

Lets consider a reaction:

$$PCl_5 (g) \rightleftharpoons PCl_3 (g) + Cl_2 (g) \qquad K = 1.8 \ @ \ 250°c$$

Determine $\Delta G°$ @ $250°C$

$\Delta G° = -8.314 \dfrac{J}{mol \cdot K} (250 + 298.5 \ K) \ln 1.8 = -2678.7 \dfrac{J}{mol}$

$[PCl_5] = 2.3\ M$
$[PCl_3] = 0.6\ M$
$[Cl_2] = 1.15\ M$

① Which direction will be spontaneous @ 250°C?

$$Q = \frac{(0.6)(1.15)}{2.3} = 0.3$$

$K > Q$ need to make more __products__

② What is the sign of ΔG?   Products are favored, so $\Delta G < 0$
(spontaneous as written)

③ Calculate ΔG. $\Delta G = \Delta G° + RT \ln Q$
$\Delta G = -4557.3 + 8.314(250 + 298.15) \ln 0.3$
$\Delta G = -10,042\ J/mol$

So... this tells us __IF__ a reaction will be spontaneous. The field of Thermodynamics explores __WHY__ a reaction is spontaneous

- The question of "why" boils down to $\underline{2}$ new and incredibly important concepts : Enthalpy (ΔH) and Entropy (ΔS)
  $\hookrightarrow$ heat $\hookrightarrow$ disorder
  $\Delta H > 0$ = endothermic $\Delta H < 0$ = exothermic

We will discuss these in a lot more detail, but for now, let's see how they relate to reaction spontaneity

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

$\Delta G < 0 \rightarrow$ spontaneous

$\Delta H < 0 \rightarrow$ contributes to a spontaneous reaction
  Enthalpically favorable

$\Delta S > 0 \rightarrow$ Entropically favorable
(helps make $\Delta G < 0$)

−	−	+	$\Delta H < 0$ + $\Delta S > 0 \rightarrow$ ALWAYS spontaneous
+	+	−	$\Delta H > 0$ + $\Delta S < 0 \rightarrow$ NEVER spontaneous
+/−	−	−	$\Delta H < 0$ + $\Delta S < 0 \rightarrow$ spontaneous at low Temp
+/−	+	+	$\Delta H > 0$ + $\Delta S > 0 \rightarrow$ spontaneous @ high temps

OK... now we have seen two important equations that involve ΔG

$$\Delta G^\circ = -RT\ln K \quad \text{and} \quad \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

combined $\longrightarrow$ $\quad -RT\ln K = \Delta H^\circ - T\Delta S^\circ$

rearranged $\longrightarrow$ $\quad \ln K = \dfrac{-\Delta H^\circ}{RT} + \dfrac{\Delta S^\circ}{R}$

We can use this expression to derive an equation that allows us to calculate how K responds to changing the Temperature

$$\ln K_1 = \dfrac{-\Delta H^\circ}{RT_1} + \dfrac{\Delta S^\circ}{R} \qquad\qquad \ln K_2 = \dfrac{-\Delta H^\circ}{RT_2} + \dfrac{\Delta S^\circ}{R}$$

$$\underbrace{\ln K_2 - \ln K_1}_{= \ln \frac{K_2}{K_1}} = \left[\dfrac{-\Delta H^\circ}{RT_2} + \dfrac{\Delta S^\circ}{R}\right] - \left[\dfrac{-\Delta H^\circ}{RT_1} + \dfrac{\Delta S^\circ}{R}\right]$$

Van't Hoff Equation

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

$$\ln \dfrac{K_2}{K_1} = \dfrac{-\Delta H^\circ}{RT_2} + \dfrac{\Delta S^\circ}{R} + \dfrac{\Delta H^\circ}{RT_1} - \dfrac{\Delta S^\circ}{R} \qquad \text{these cancel}$$

$$\ln \dfrac{K_2}{K_1} = \dfrac{-\Delta H^\circ}{RT_2} + \dfrac{\Delta H^\circ}{RT_1} = \dfrac{\Delta H^\circ}{R}\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)$$

Let's rationalize this conceptually: $\qquad \Delta H < 0 \longrightarrow$ exothermic

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad -$ heat is a Product

exothermic: $\quad A + B \rightleftharpoons C + $ heat

$\qquad$ @ low temp [heat] is small so reaction favors products ($\uparrow$ K)

$\qquad$ @ high temp [heat] is large. Reaction will favor more reactants ($\downarrow$K)

$\qquad\qquad$ So, when $\Delta H < 0$ K increases as temperature decreases

Endothermic: heat + A + B ⇌ C
    ↳ heat is a reactant

↓T = ↓[heat]   so reactants are favored → small K

↑T = ↑[heat]   products are favored → high K

when $\Delta H > 0$, K increases with Temperature

Sample Problem:

The equilibrium constant for the synthesis of methane has been determined at two temperatures. Determine $\Delta H°$ for this reaction.

773.15 K   500 °C $K_P = 2.69 \times 10^3$ atm^{-1}
1173.15 K 900 °C $K_P = 51.43$ atm^{-1}

Conceptually, what do we expect? $\Delta H > 0$ or $\Delta H < 0$
        low temp = larger K
        high temp = lower K

    heat + react ⇌ prod .... ↑T would ↑K

        K decreases with ↑T
            heat must be a product → exothermic

$$\ln \frac{51.43}{2690} = \frac{\Delta H°}{8.314} \left(\frac{1}{773.15} - \frac{1}{1173.15} \right)$$

$$-3.957 = \frac{\Delta H°}{8.314} (0.000441)$$

Yep!

$$\Delta H° = -74,600 \frac{J}{mol}$$