Manipulating Reactions and the Effect on K

1. Stoichiometric Coefficients: If you multiply the coefficients in the equation by a factor, raise the equilibrium constant to the same factor to get the equilibrium constant for the reaction.

$$2\,X + Y \leftrightarrow 2\,Z \qquad K$$

$$X + \frac{1}{2} Y \leftrightarrow Z \qquad K^{\frac{1}{2}}$$

$$4\,X + 2\,Y \leftrightarrow 4\,Z \qquad K^2$$

2. Reversing Equations: When the equation is written in reverse, take the reciprocal of K to get the equilibrium constant for the reaction.

$$2\,X + Y \leftrightarrow 2\,Z \qquad K$$

$$2\,Z \leftrightarrow 2\,X + Y \qquad \frac{1}{K}$$

3. Adding Equations: If you add two or more chemical equations to get the overall reaction (like in Hess's Law), multiply the respective K's to get the equilibrium constant for the reaction.

$$K_{total} = K_1 \times K_2 \times K_3 \ldots$$

Let's Practice!

1. The Haber Process is a famous industrial method for producing ammonia from nitrogen and hydrogen gases:

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) \qquad K_c = 3.8 \times 10^4 \text{ at } 127°C$$

a. Calculate the value of the equilibrium constant, K_c, at 127°C for the reaction: $2\,NH_3(g) \rightleftharpoons N_2(g) + 3\,H_2(g)$ reverse!

$$K' = \frac{1}{K} = \frac{1}{3.8E4} = \boxed{2.6 \times 10^{-5}}$$

b. Calculate the value of K_c at 127°C for this reaction: $\frac{1}{2} N_2(g) + 3/2\,H_2(g) \rightleftharpoons NH_3(g)$ $\times \frac{1}{2}$

$$K' = K^{1/2} = \sqrt{3.8E4} = \boxed{190}$$

c. Calculate the value of K_c at 127°C for this reaction: $6\,NH_3(g) \rightleftharpoons 3\,N_2(g) + 9\,H_2(g)$ reverse $\times$ 3

$$K' = \frac{1}{K^3} = \frac{1}{(3.8E4)^3} = \boxed{1.8 \times 10^{-14}}$$

THE REACTION QUOTIENT, Q: When you need to know the answer to the question, "Is the system at equilibrium?"

A: The answer can be yes or no!

For the general reaction: aA + bB ⇌ cC + dD

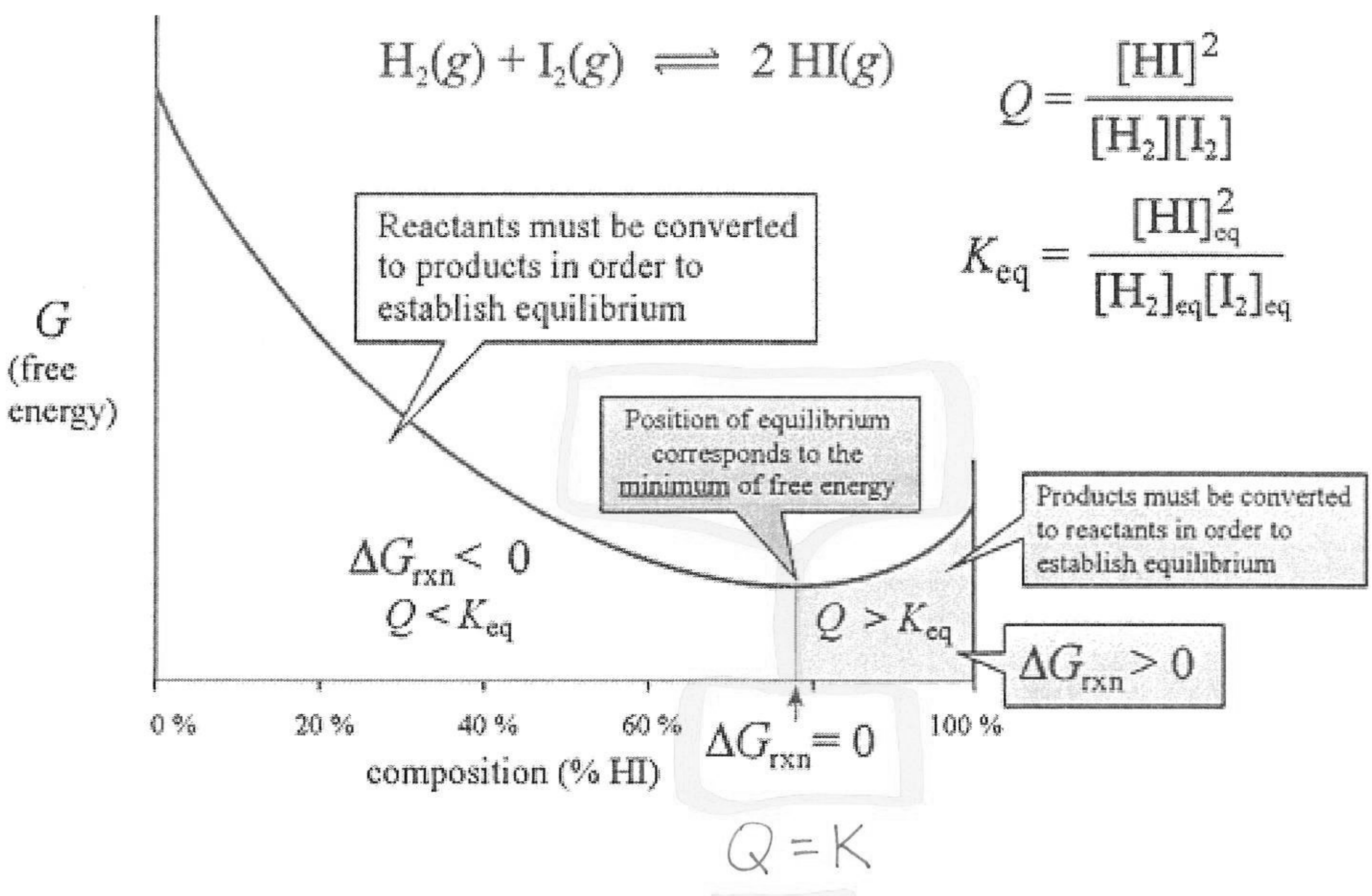
$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b} \quad \text{or} \quad \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b}$$

Reminder:

- Q has the appearance of K (same exact ratio!)
- But... Q can be calculated at any point in the reaction progress, not only at equilibrium!

What does *Q* mean?

1. If *K* > *Q*, system not at equilibrium: forward reaction is favored (shift right) to make Q = K.
2. If *K* ≈ *Q*, the system is at equilibrium.
3. If *K* < *Q*, system not at equilibrium: reverse reaction is favored (shift left) to make Q = K.



The Kinetics of Equilbrium

1. If equilibrium is approached from the left (starting with reactants), $K > Q$, $-\Delta G$
   a. the rate of the forward reaction ↓ to a constant, non-zero rate (i.e. it slows down over time until equilibrium is reached).
   b. the rate of the reverse reaction ↑ to a constant, non-zero rate (i.e. it speeds up over time until equilibrium is reached).
2. If equilibrium is approached from the right (starting with products), $K < Q$, $+\Delta G$
   a. the rate of the forward reaction ↑ to a constant, non-zero rate (i.e. it speeds up over time until equilibrium is reached).
   b. the rate of the reverse reaction ↓ to a constant, non-zero rate (i.e. it slows down over time until equilibrium is reached).
3. Time required to reach equilibrium does NOT depend on the equilibrium constant, *K*!
4. Regardless of initial conditions, at a given temperature a reaction will reach equilibrium with the same ratio of products to reactants.

In Summary

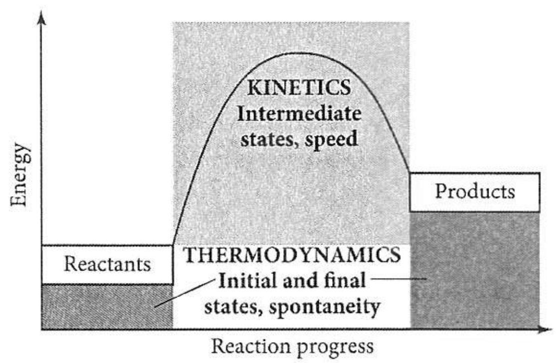
Current conditions	$K > Q$	$K \approx Q$	$K < Q$
change needed for system to reach equilibrium	shift right (make more products)	already at equilibrium	shift left (make more reactants
reaction rates	forward > reverse reaction rate (until equilibrium reached)	forward ≈ reverse reaction rate	forward < reverse reaction rate (until equilibrium reached)

Thermodynamics:

- Will a reaction happen spontaneously?
- Determined by ΔG (i.e., combo of ΔH and ΔS) — and K! (b/c $\Delta G = -RT\ln K$)

Kinetics:

- How fast will a reaction happen?
- Determined by activation energy, E_a, and temperature



Equilibrium vs Kinetics: k vs *K*!

Equilibrium	Kinetics
K = equilibrium constant no units!	*k* = rate constant lots of units $M^{1-p}\ time^{-1}$

What we **can** determine about *k* using *K*:

- Relative rates of forward and reverse reactions (by comparing K vs Q)

What we **can't** determine about *k* using *K*:

- Absolute rates of forward and reverse reactions

You CANNOT compare the rate of one reaction to another by comparing their *K* values! ↑ K_{eq}