Chemical Equilibria

Why do we care?!!

Predicting

Chemistry

Put stuff in a beaker and what do you get?

We can use thermodynamics to predict the molecular concentrations at equilibrium (very powerful!)

Low G

$$2H_2O(g) \longleftrightarrow 2H_2(g) + O_2(g)$$

Products
High G

298 K

ALL R

$\Delta_r G° = +113.4$ kJ mol^{-1}

$$e^{-\Delta_r G°/RT} \longrightarrow e^{-45} \approx 10^{-20}$$

What about the opposite reaction?

$$2H_2(g) + O_2(g) \longleftrightarrow 2H_2O(g)$$

$\Delta_r G° = -113.4$ kJ mol^{-1}

$$e^{-\Delta_r G°/RT} \longrightarrow e^{+45}$$

ALL P

$$10^{20}!$$

Does everything go to equilibrium as predicted?

What happens if you mix H_2 and O_2 at 298K?

A. The explode and form water

B. They explode and form hydrogen peroxide (H_2O_2)

C. Nothing

NEED A MATCH

Why didn't I get to equilibrium?

Kinetics	Other Reactions
Too slow	$2C + O_2 \rightarrow 2CO$
We might not get to equilibrium	OR
	$C + O_2 \rightarrow CO_2$
	MAYBE BOTH

Chemical Equilibria

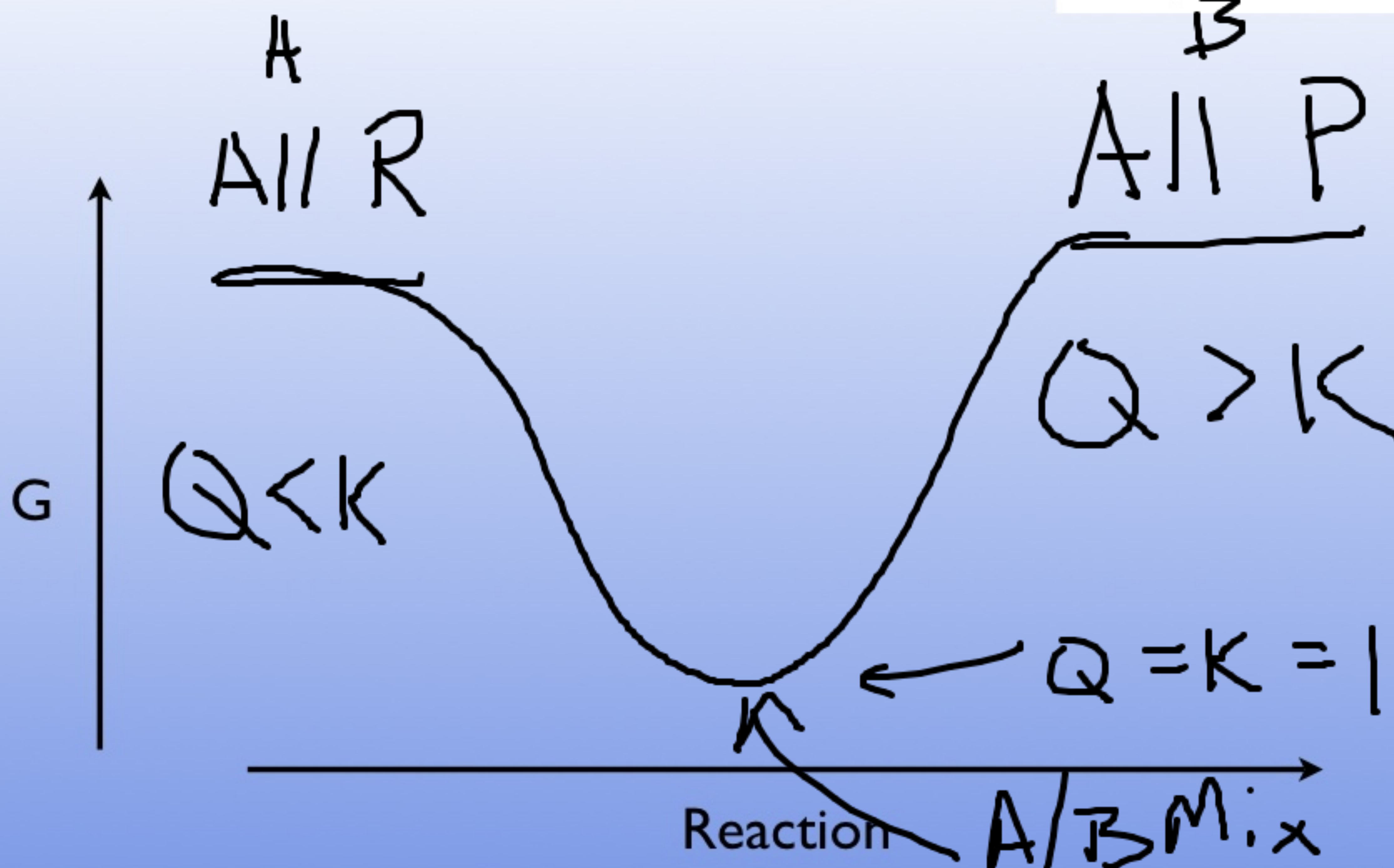
Why do we care?!!

Things might not get to equilibrium but they never move away from it

Why does K depend on $\Delta_r G°$?

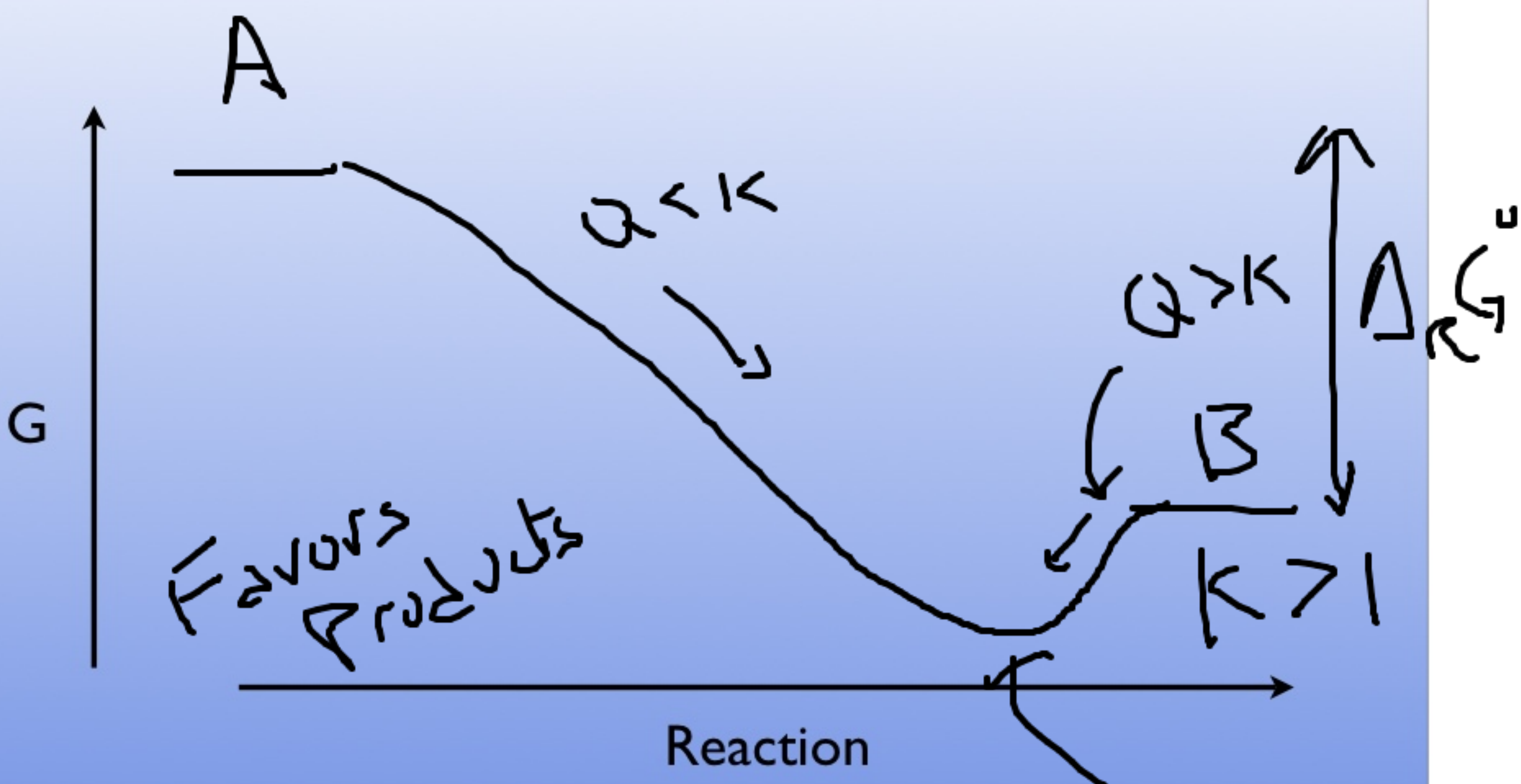
$$A \longleftrightarrow B$$

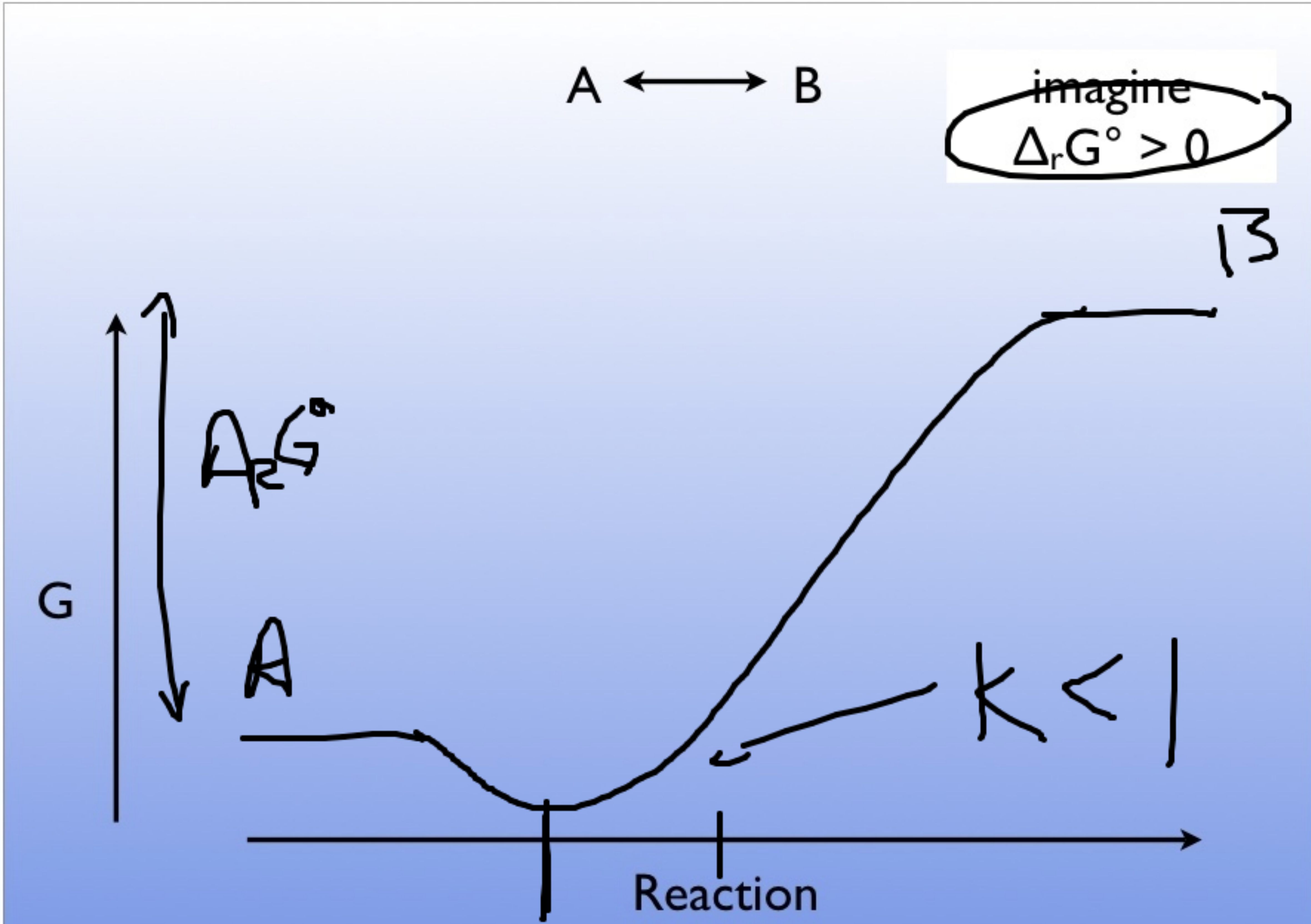
imagine
$\Delta_r G° = 0$



A ⟷ B

imagine
$\Delta_r G^\circ < 0$





A ⟷ B
imagine
$\Delta_r G° > 0$
G
Reaction
$\Delta_r G°$
A
B
K < 1

Equilibrium does not depend on starting conditions

TABLE 6.1 Results of Three Experiments for the Reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

Experiment	Initial Concentrations	Equilibrium Concentrations	$K = \frac{[NH_3]^2}{[N_2][H_2]^3}$
I	$[N_2]_0 = 1.000\ M$ $[H_2]_0 = 1.000\ M$ $[NH_3]_0 = 0$	$[N_2] = 0.921\ M$ $[H_2] = 0.763\ M$ $[NH_3] = 0.157\ M$	$K = 6.02 \times 10^{-2}\ L^2/mol^2$
II	$[N_2]_0 = 0$ $[H_2]_0 = 0$ $[NH_3]_0 = 1.000\ M$	$[N_2] = 0.399\ M$ $[H_2] = 1.197\ M$ $[NH_3] = 0.203\ M$	$K = 6.02 \times 10^{-2}\ L^2/mol^2$
III	$[N_2]_0 = 2.00\ M$ $[H_2]_0 = 1.00\ M$ $[NH_3]_0 = 3.00\ M$	$[N_2] = 2.59\ M$ $[H_2] = 2.77\ M$ $[NH_3] = 1.82\ M$	$K = 6.02 \times 10^{-2}\ L^2/mol^2$

Each equilibrium has different concentrations, but the same value for Kc

A convention to keep things straight

we'll be doing a lot of aqueous problems
C denote concentrations initially
[ ] denote concentrations at equilibrium

Reaction	$3H_2(g)$ +	$N_2(g)$ $\longleftrightarrow$	$2NH_3(g)$
Initial	C_{H_2}	C_{N_2}	C_{NH_3}
Change	$-3x$	$-x$	$+2x$
Equilibrium	$[H_2]$	$[N_2]$	$[NH_3]$

$$[NH_3] = C_{NH_3} + 2x$$

Really Easy problems

At equilibrium you find

$[H_2]$ = .1 M, $[N_2]$ = 0.2 M, and $[NH_3]$ = .2M

$$K = \frac{[NH_3]^2}{[H_2]^3[N_2]} = \frac{(.2)^2}{(.1)^3(.2)} = 200$$

Reaction	$3H_2(g) + N_2(g) \longleftrightarrow 2NH_3(g)$		
Initial			
Change			
Equilibrium	.1	.2	.2 → K

Fairly Easy problem

Given K = 200 and
$[H_2]$ = .2 M, $[N_2]$ = 0.4 M, and C_{NH_3} = .1M
fill in the rest

$$K = \frac{[NH_3]^2}{[H_2]^3[N_2]} \Rightarrow [NH_3] = 0.8$$

Reaction	$3H_2(g)$ +	$N_2(g)$ $\longleftrightarrow$	$2NH_3(g)$
Initial			.1
Change			+.7 = 2x x = .35
Equilibrium	.2	.4	.8 from K

Typical problem

Given K = 200 and
C_{H2} = .2 M, N_2 = 0.2 M what are the concentrations at equilibrium

Reaction	$3H_2(g) + N_2(g)$	$\longleftrightarrow$	$2NH_3(g)$
Initial	.2	.2	0
Change	−3x	−x	+2x
Equilibrium	.2 − 3x	.2 − x	+2x

→ K

$$K = \frac{(2x)^2}{(.2-3x)^3(.2-x)} = 200$$

ALGEBRA $\longrightarrow$ $x = 0.045$

Reaction	$3H_2(g)$ +	$N_2(g) \longleftrightarrow$	$2NH_3(g)$
Initial	.2	.2	0
Change	-3x	-x	+2x
Equilibrium	.2-3x	.2-x	+2x

I thought you said we need to use
K_p for gases
and
K_c for solutions?

STD!

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

Std for GAS P → K_p

Std for sol'n [ ] → K_c

Relating K_p and K_c

$$2NO_2(g) \longrightarrow N_2O_4(g)$$

$$K_c = \frac{[N_2O_4]}{[NO_2]^2} \qquad K_p = \frac{P_{N_2O_4}}{P_{NO_2}}$$

$$P_{N2O4} = \frac{n_{N_2O_4}}{V} RT$$

atm

L

L-atm K^{-1} mol^{-1}

$[N_2O_4]$

Relating K_p and K_c

$$2NO_2(g) \longrightarrow N_2O_4(g)$$

$$K_p = \frac{P_{N2O4}}{P_{NO2}{}^2} = \frac{[N_2O_4]RT}{[NO_2]^2(RT)^2} = K_c \times \frac{1}{RT}$$

K_c

In general $K_P = K_c(RT)^{\Delta n}$

Δn is the change in the number of moles of gas

$\Delta n = n_f - n_i = 1 - 2 = -1$

Time out for activities

That is what we are actually putting into the equilibrium constant

Gas

$$a_i = \frac{P_i}{P^o} = P_i$$

(P^o = 1 atm)

Free Energy Changes with P

Compound in solution

$$a_i = \frac{[i]}{[c^o]} = [i]$$

($[c^o]$ = 1 M)

Free Energy Changes with Concentration

What about the activity of a pure liquid or solid?

The pure compound is the reference state!

$$a_i = \frac{\text{pure solid}}{\text{pure solid}} = 1$$

Pure solids and liquids "don't show up"
in the equilibrium constant
(they are there. they are just always = 1)

What is the equilibrium constant for this reaction?

$$H_2O(l) \longleftrightarrow H_2O(g)$$

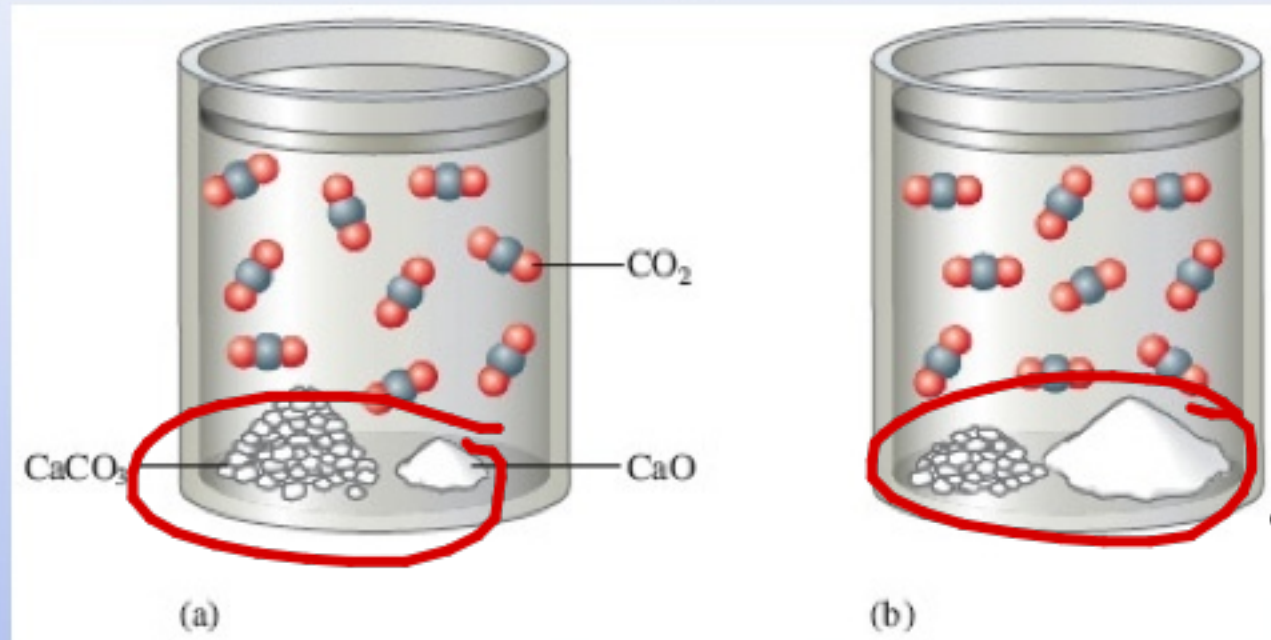
$$K = \frac{P_{H_2O}}{a_{H_2O(l)}} = P_{H_2O}$$

1

only one P!

VAPOR P

Equilibria with more than one phase are called Heterogeneous Equilibria



same P

amount solid doesn't matter

$CaCO_3(s) \leftrightarrow CaO(s) + CO_2(g)$

$$K = \frac{a_{CaO}^{1} \, P_{CO_2}}{a_{CaCO_3}^{1}} = P_{CO_2}$$

For the following reaction $\Delta_R G° = +740\ kJ\ mol^{-1}$ at 298K
In air will I form any solid iron?

$$Fe_2O_3(s) \longrightarrow 2Fe(s) + (3/2)O_2(g)$$

A. all the iron oxide will convert to iron

B. about half of the iron oxide will convert to iron

C. a very small amount of the iron oxide will convert to iron

D. not a single atom of iron will form

$P_{O_2} = .2$ atm

TOO MUCH O_2

For the following reaction $\Delta_R G° = +740$ kJ mol^{-1} at 298K
In air will I form any solid iron?

$$Fe_2O_3(s) \longrightarrow 2Fe(s) + (3/2)O_2(g)$$

$$K = \exp[-740{,}000/(8.314)(298)] = 2 \times 10^{-130}$$

What is Q?

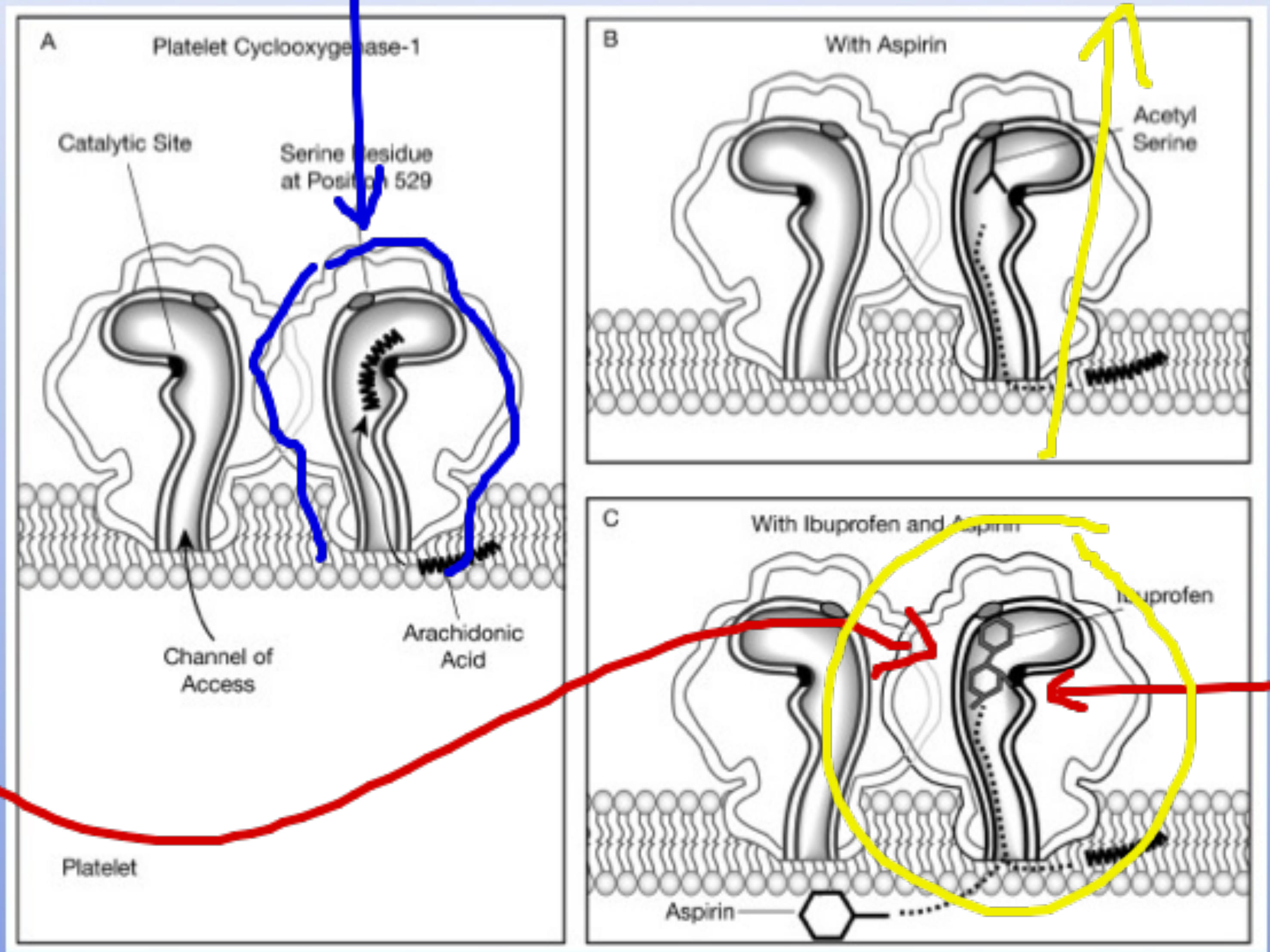
$$Q = (P_{O_2})^{3/2} = (.2)^{3/2} = 0.09$$

$$Q \gg K$$

Always too much O_2 in air.

What is equilibrium good for?

Drug + Protein ⟷ Drug-Protein Complex



Fendrick *et al.* *Osteopathic Medicine and Primary Care* 2008 **2**:2 doi:10.1186/1750-4732-2-2

Drug Binding
How "strongly" should it bind to work?

Drug + Protein $\longleftrightarrow$ Drug-Protein Complex

$$K = \frac{[\text{complex}]}{[\text{Drug}][\text{protein}]}$$

free (→ [protein])

Do an experiment
Measure K

Drug + Protein $\longleftrightarrow$ Drug-Protein Complex

For ibuprofin binding to the COX channel

$K \sim 10^8$

If we want 100x more complexed protein than free protein what concentration of drug do we need?

A. 10^{-8} M

B. 10^{-6} M

C. 10^{-4} M

D. 10^{-2} M

$$K = \frac{[complex]}{[drug][protein]}$$

100

$$[Drug] = \frac{100}{K}$$

How much is that?

$[\text{complex}] \ll [\text{Drug}]$

Person is 50 kg = 50 L of water

MW of ibuprofin is ~200 g mol^{-1}

$[\text{Drug}] = \text{Total Dose}$

$$[\text{Drug}] = 10^{-6}\,M \times 50\,L$$

$$= 5 \cdot 10^{-5}\,\text{mol} \times 200\,\text{g mol}^{-1}$$

$$= 10\,\text{mg}$$

For the following reaction what is the change value for H_2O?

$$2C_2H_6(g) + 7O_2(g) \longrightarrow 4CO_2(g) + 6H_2O(g)$$

R	C_2H_6	O_2	CO_2	H_2O
I	1.0	1.4	1.8	0
C	-2x	?	?	?

A. -2x

B. +2x

C. +3x

D. +6x

For the following reaction what is the equilibrium value for CO_2?

$$2C_2H_6(g) + 7O_2(g) \longrightarrow 4CO_2(g) + 6H_2O(g)$$

R	C_2H_6	O_2	CO_2	H_2O
I	1.0	1.4	1.8	0
C	-2x	?	?	?

A. 1.8 - 2x

B. 1.8 + 2x

C. 1.8 + 4x

D. 1.0 + 6x