Chemical Equilibria

"Stress"

Temp

changes K

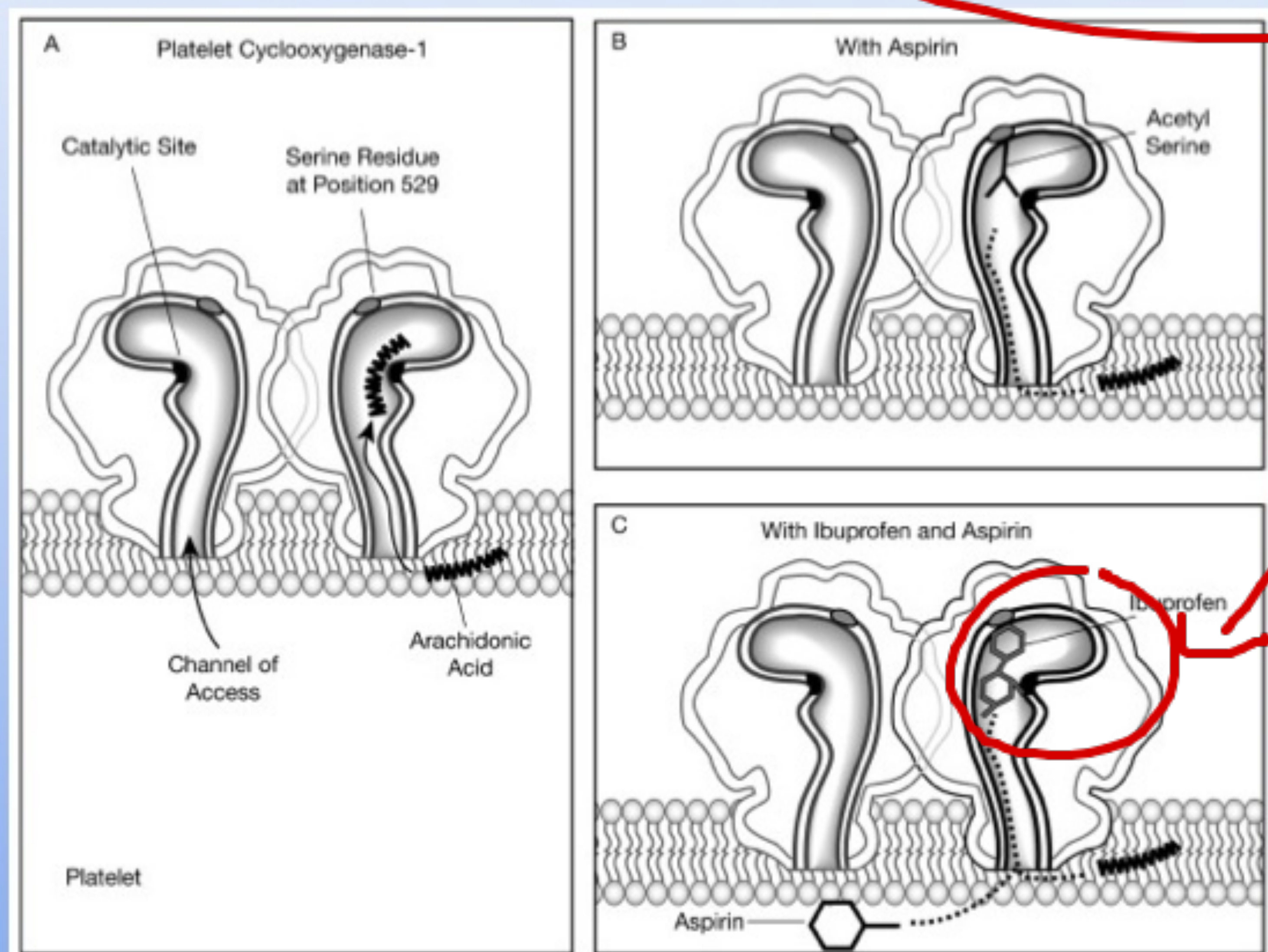
What happens when we try to change a chemical system at equilibrium?

concentration

pressure

What is equilibrium good for?

Drug + Protein $\longleftrightarrow$ Drug-Protein Complex



Blocks Active Site

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

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 "free" drug do we need?

A. 10^{-8} M

B. 10^{-6} M

C. 10^{-4} M

D. 10^{-2} M

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

$= 100$

$$[\text{DRUG}] = \frac{100}{K} = 10^{-6} \text{ M}$$

What is the initial concentration of Drug?

Drug + Protein $\longleftrightarrow$ Drug-Protein Complex

Given that K = 10^8 and the initial concentration of protein is 10^{-8} M

What is the maximum concentration that we can expect for the ~~drug~~? COMPLEX

A. 10^{-8} M

B. 10^{-6} M

C. 10^{-4} M

D. 10^{-2} M

All of it !

Can't be more

What is the initial concentration of Drug?

Reaction Drug + Protein $\longleftrightarrow$ Drug-Protein Complex

	Drug	Protein	Drug-Protein Complex
Initial	$10^{-6} + x$	10^{-8}	0
Change	$-x$	$-x$	$+x$
Equilibrium	10^{-6}	~ 0	10^{-8}

10^{-8}

+

~SAME

assume it all forms complex

What will happen if I add more drug after my initial equilibrium?

A. more drug will bind

B. less drug will bind

C. an identical amount of drug will stay bound

D. the system will go back to equilibrium and all the concentration will return to the same values

Since the equilibrium concentration of the drug is essentially the equilibrium concentration we can easily find the new equilibrium ratio of the complex: free protein

Drug + Protein $\longleftrightarrow$ Drug-Protein Complex

First Equilibrium
[Drug] = 10^{-6} M

$$10^8 \;\cancel{K} = \frac{1}{10^{-6}} \frac{[\text{complex}]}{[\text{protein}]} = 100$$

Equilibrium after adding drug
[Drug] = 10^{-4} M

$$K = \frac{1}{10^{-4}} \frac{\text{complex}}{\text{protein}} = 10^4!$$

Equilibria and Perturbations (Stress)

What happens to a system at equilibrium
if I change something like

The concentrations
of one of the chemicals

The Pressure

K const

The Temperature ← K changes

Qualitatively Understanding "stress"

Le Chatlier's Principle

If a chemical system at equilibrium experiences a change,

then the equilibrium shifts to partially counter-act the imposed change.

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

You find the system at equilibrium,
then you decide to add more H_2 to the mixture

What happens as the reaction goes to a new equilibrium?

A. the concentration of N_2 decreases

B. the concentration of NH_3 decreases

C. nothing when equilibrium is reached all the concentrations will the same as before

$H_2 \uparrow$

TO PROD

Stressing the concentrations

Add Reactants $\longrightarrow$ Reaction Shifts towards Product

Add Products $\longrightarrow$ Reaction Shifts towards Reactants

Amount of pure substances doesn't matter

What if I increase the pressure?

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

You find the system at equilibrium at 1 atm,
then you decide to increase the pressure to 2 atm.

What happens as the reaction goes to a new equilibrium?

A. moves towards the products as they have fewer molecules

B. moves towards the reactants as they have more molecules

C. moves towards the products as they have a lower free energy

Relieve stress. Lower P. fewer n

Dealing with Stress from a Quantitative Perspective

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

Equilibrium

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$[N_2] = 0.921$ M
$[H_2] = 0.763$ M
$[NH_3] = 0.157$ M

$$K_c = \frac{[0.157]^2}{[.921][.763]^3} = \underline{0.06}$$

If I increase $[N_2]$ to 3 M the system will no longer be at equilibrium.
Which way will it shift to get back to equilibrium?

WHAT IS Q?

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

Not at equilibrium

C_{N_2} → $[N_2] = 3\ M$

C_{H_2} → $[H_2] = 0.763\ M$

C_{NH_3} → $[NH_3] = 0.157\ M$

not at equilibrium

$$Q = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$$Q = \frac{[0.157]^2}{[3][.763]^3} = .0185$$

$Q = 0.0185$

$K = 0.06$

$Q < K$

therefore reaction needs to increase products to get to equilibrium

"Too few products"

K is constant

$$K = \frac{\text{Products}}{\text{Reactants}}$$

So if products goes up
the reaction will shift to get
back to the same constant ratio

This can happen if
Product goes down slightly
and Reactant goes up slightly

Increasing Pressure

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

$$K_p = \frac{P_{N2O4}}{P_{NO2}^2} = \frac{X_{N_2O_4}\,P}{(X_{NO_2}\,P)^2} = \boxed{\frac{X_{N_2O_4}}{X_{NO_2}}}\boxed{\frac{1}{P}} = K$$

const

If you increase P
Then the mole fraction of NO2
must go down since K is constant

How to change the pressure (constant T)

Increase P (decrease V)	Shifts to side with fewer gas molecules
Decrease P (increase V)	Shifts to side with more gas molecules

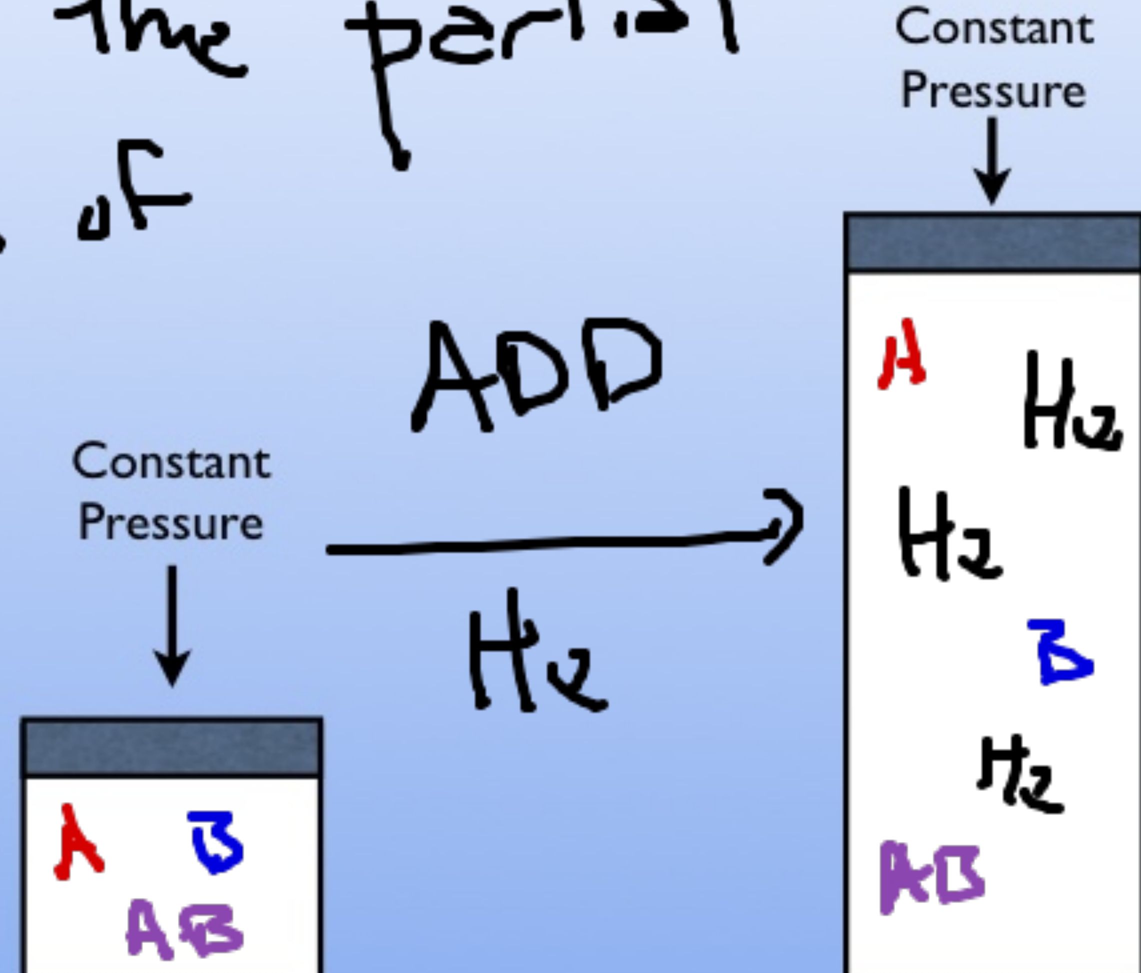
Must be gas.

Same # of molecules → No effect

Adding Inert Gas at Constant Pressure

$A(g) + B(g) \longleftrightarrow AB(g)$

Lowers the partial pressures of A, B, AB



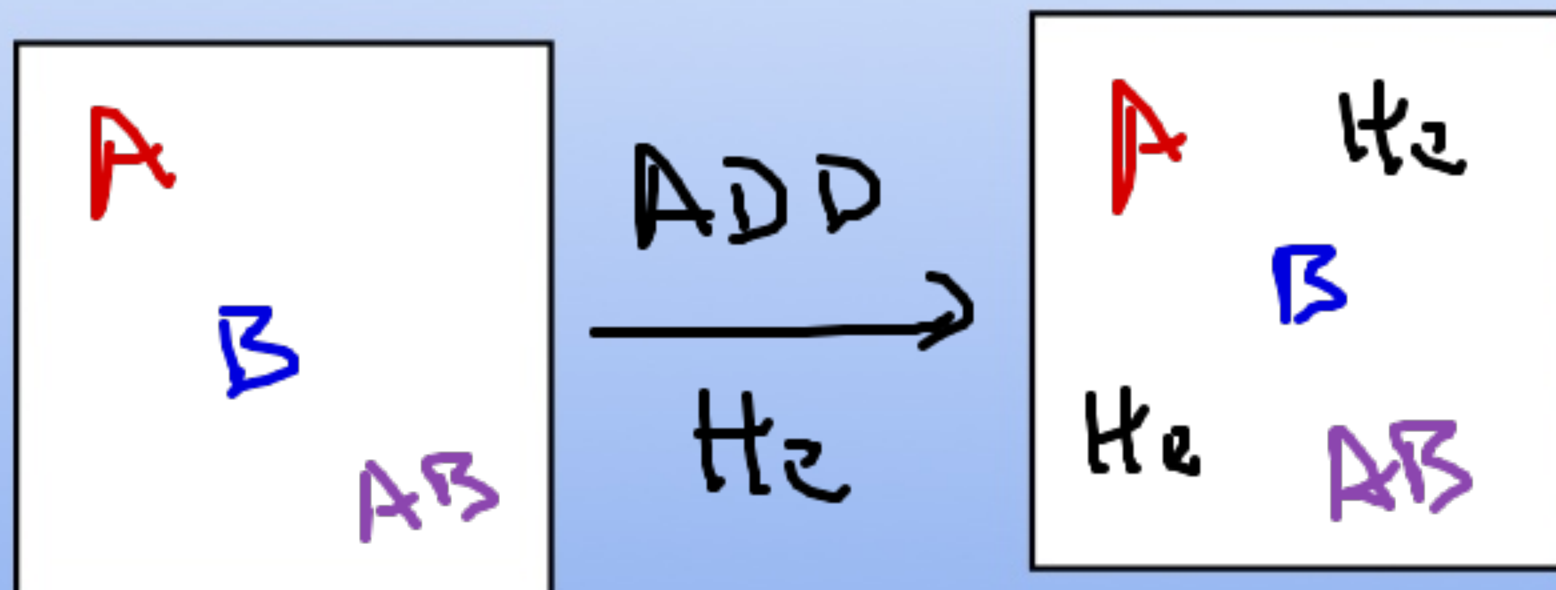
Effectively Dilutes the Gas

"Like lowering the P!"

Adding Inert Gas at Constant Volume

$A(g) + B(g) \longleftrightarrow AB(g)$

Partial P of A, B, AB unchanged.



NO EFFECT

Effectively Does nothing

Temperature Change

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g) + \text{heat}$$

this reaction is exothermic $\Delta H < 0$

If you increase T then to "partially compensate" the reactions shifts to the reactants (consuming heat)

T dependence given by ΔH

Why does Temperature Change Equilibrium?

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g) + \text{heat}$$

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

K is a function of T!

$$\Delta_R G^\circ(T) = -RT \ln K$$

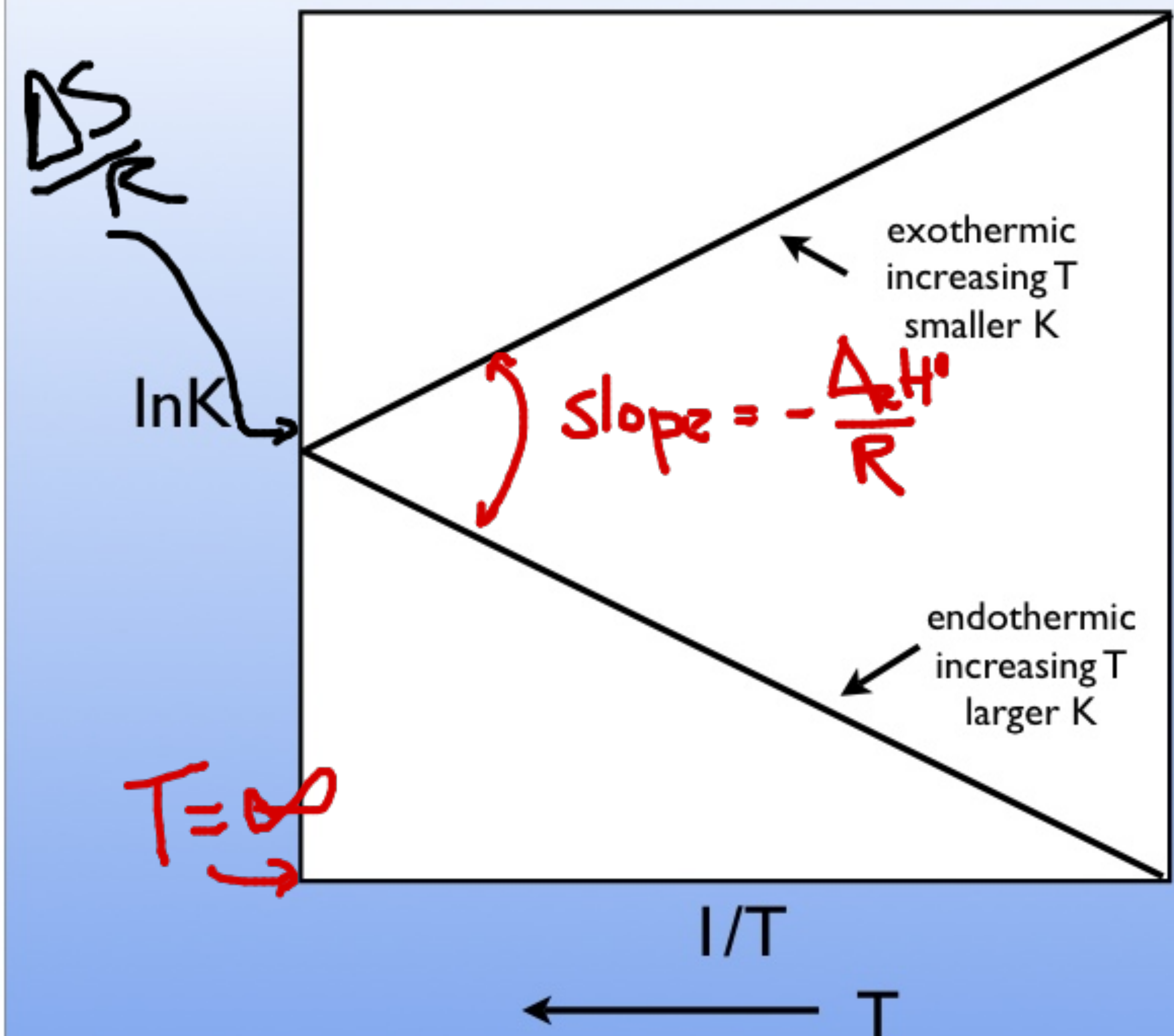
$$\Delta_R G^\circ(T) = \Delta_R H^\circ - T\,\Delta_R S^\circ$$

$$-RT \ln K = \Delta_R H^\circ - T\Delta_R S^\circ$$

$$\ln K = -\frac{\Delta_R H^\circ}{\underline{\underline{RT}}} + \frac{\Delta_R S^\circ}{R}$$

Temperature dependence of K depends on $\Delta_R H^\circ$

$$\ln K = -\Delta_R H°/RT + \Delta_R S°/R$$



$y = mx + b$

y is $\ln K$

x is $1/T$

m is $-\Delta_R H°/R$

b is $\Delta_R S°/R$

a different way to do calorimetry

measure K to find $\Delta_R H°$

Just like Classsius - Clayeron !!

Can we relate two K's at two Temperatures?

$$\ln K_2 = -\frac{\Delta_R H}{RT_2} + \cancel{\frac{\Delta_R S^\circ}{R}}$$

$$- \quad \ln K_1 = -\frac{\Delta_R H^\circ}{RT_1} + \cancel{\frac{\Delta_R S^\circ}{R}}$$

$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta_R H^\circ}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$