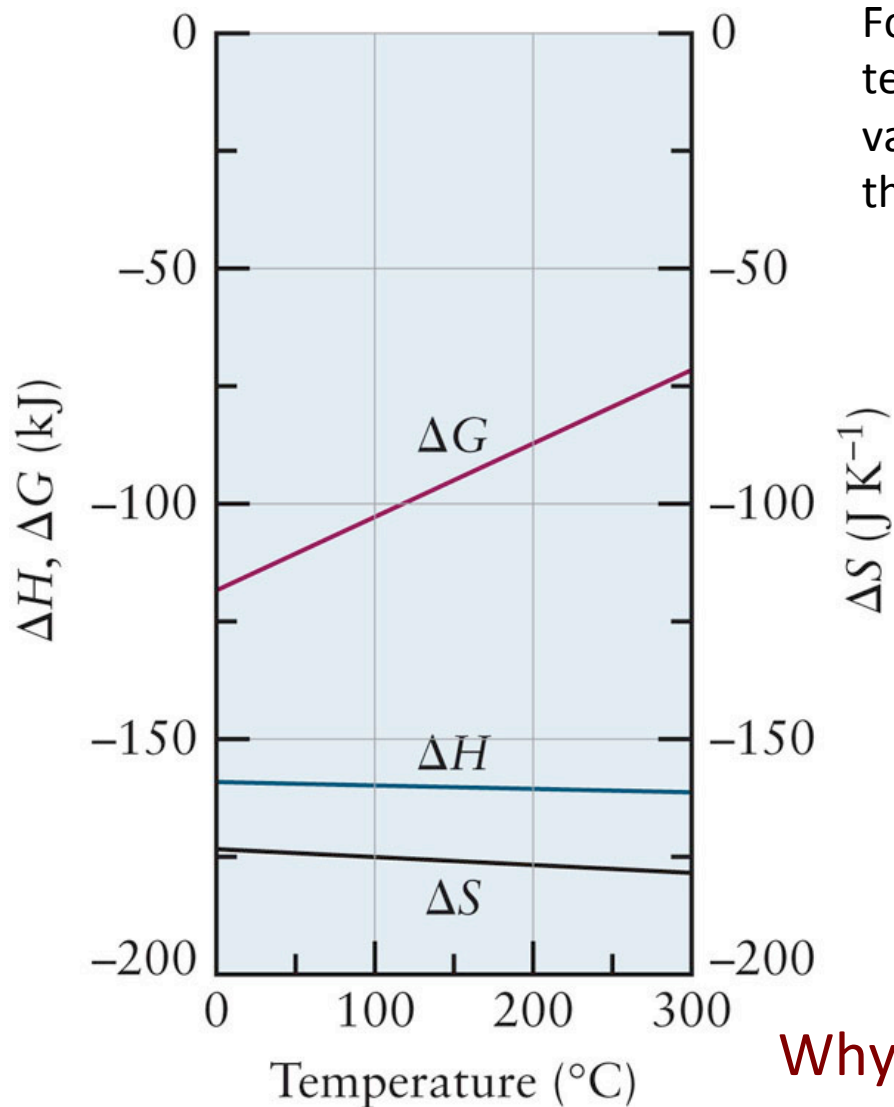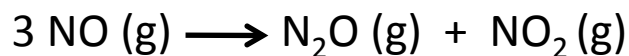# Ch 1b Lecture 16
February 12ᵗʰ, 2013

Next few lectures – OK, let's do some actual chemistry!

Today: Spontaneous Process & Equilibrium, Part II
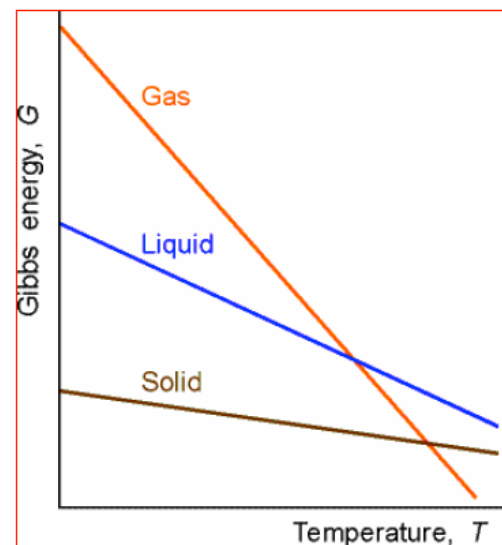
Reading: OGC Chapter 14, Sections 14.3-14.7

The Gibbs Free Energy, or $G = H - TS$

$$3\ NO\ (g) \longrightarrow N_2O\ (g)\ +\ NO_2\ (g)$$

For gases, neither ΔH or ΔS is all that temperature sensitive, and so the variation in ΔG is determined mostly by the *entropy* term.

Gases exhibit the largest T dependence, followed by liquids and then by solids.

Why is ΔS <0?

Why should this be so? Think about the statistical definition of entropy, $S = k_B \ln \Omega$.

The Gibbs Free Energy, or *G*, and Equilibrium:

With these tools in hand, we can now, at last, consider the *equilibrium* nature of chemical reactions. The equations we want to get to for a general chemical reaction are:
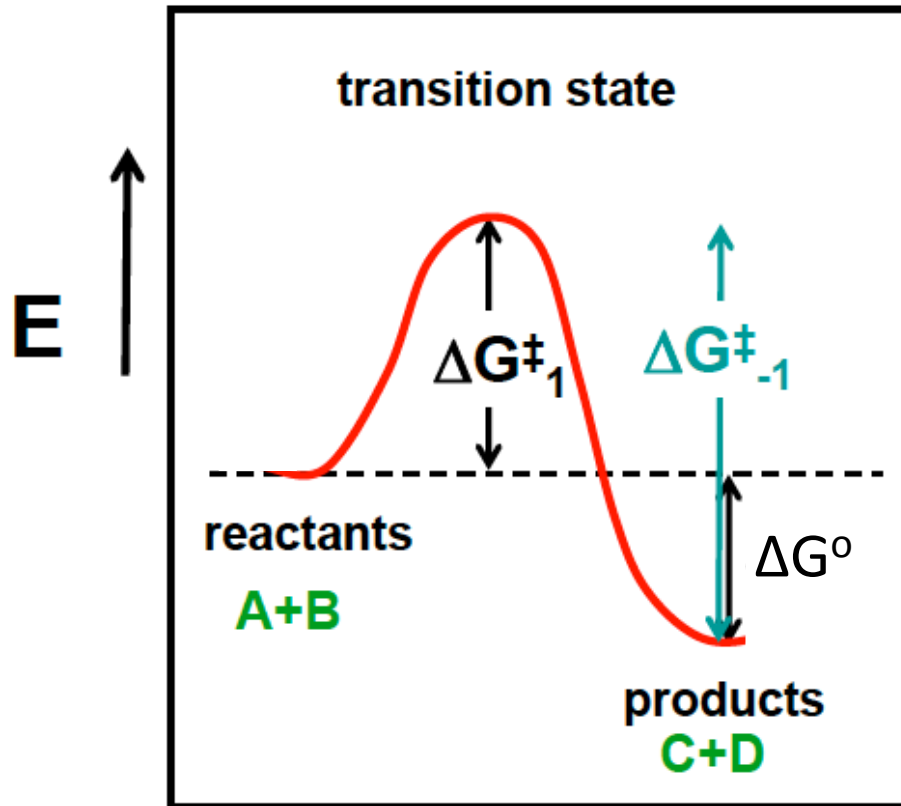
$$aA + bB \rightleftharpoons cC + dD$$

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

Law of Mass Action

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Reaction Coordinates

For the reaction aA + bB ⇔ cC + dD

$$K = \frac{[C]_{eq}^{c}[D]_{eq}^{d}}{[A]_{eq}^{a}[B]_{eq}^{b}}$$

In solution, $K = K_C$
& has units of [concentration]$^{c+d-a-b}$
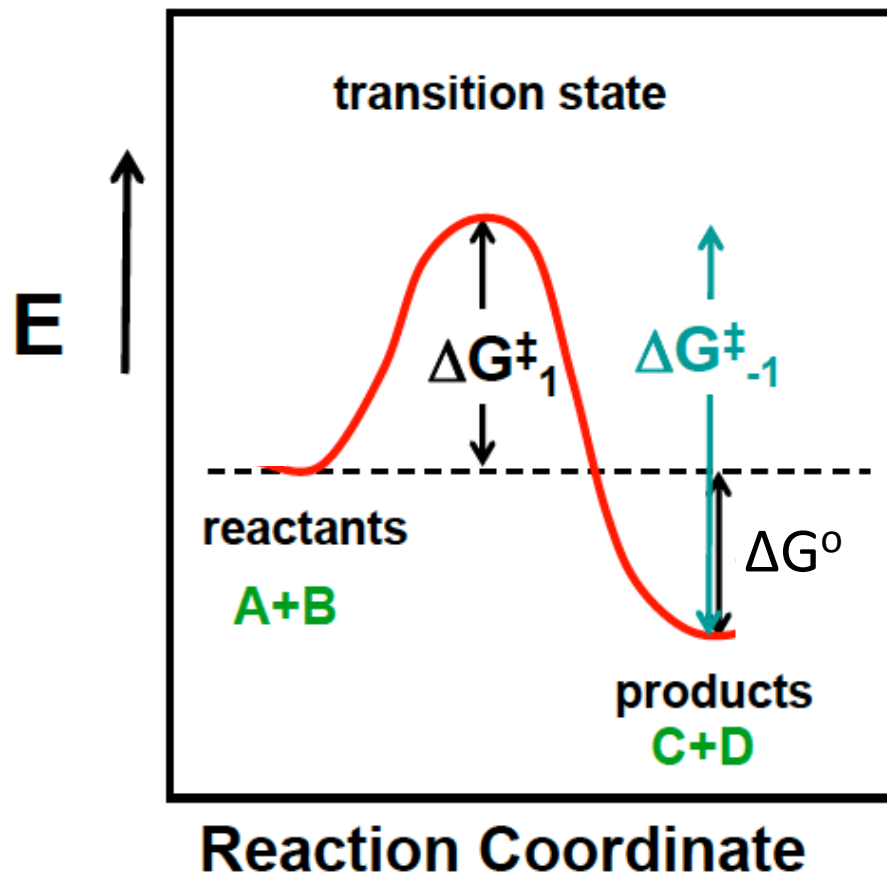
In the gas phase, $K = K_P$
& has units of [pressure]$^{c+d-a-b}$

Here we will focus on gas phase equilibria, but the arguments we make are general.

Equilibrium and ΔG^o

For the <u>gas phase</u> reaction aA + bB ⇔ cC + dD

transition state

E

$\Delta G^{\ddagger}_1$ $\Delta G^{\ddagger}_{-1}$

reactants

ΔG^o

A+B

products
C+D

Reaction Coordinate

$$K_P = \frac{[P_C]^c_{eq}[P_D]^d_{eq}}{[P_A]^a_{eq}[P_B]^b_{eq}}$$

Assume
- all products and reactants are ideal gases,
- the initial pressure is P_1,
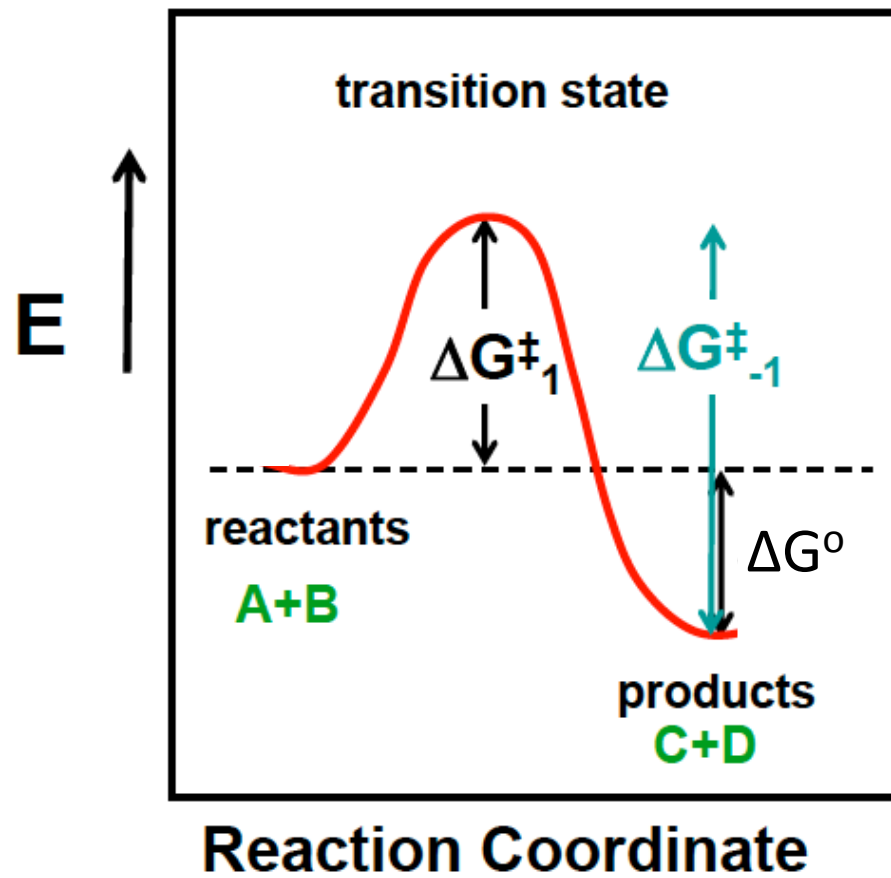- the final pressure is P_2,
- $\Delta T = 0$; T=298K

Then

$\Delta G = \Delta(H-TS) = \Delta H - T\Delta S$ 0

$\Delta H = 0$ (isothermal process)

Equilibrium and ΔG^o

For the <u>gas phase</u> reaction aA + bB ⇔ cC + dD

transition state

$\Delta G^{\ddagger}_1$ $\Delta G^{\ddagger}_{-1}$

E

reactants
A+B

ΔG^o

products
C+D

Reaction Coordinate

$$K_P = \frac{[P_C]^c_{eq}[P_D]^d_{eq}}{[P_A]^a_{eq}[P_B]^b_{eq}}$$

$\Delta G = - T\Delta S$

From previous lectures

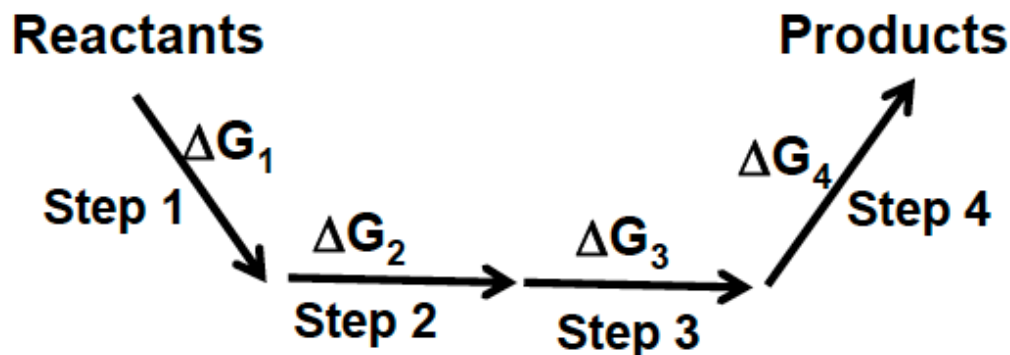$$\Delta S = nR\ln\left(\frac{V_2}{V_1}\right) = -nR\ln\left(\frac{P_2}{P_1}\right)$$

And so:

$$\Delta G = -T\Delta S = nRT\ln\left(\frac{P_2}{P_1}\right)$$

Equilibrium and ΔG^o

For the <u>gas phase</u> reaction aA + bB $\Leftrightarrow$ cC + dD

$$\Delta G = -T\Delta S = nRT \ln\left(\frac{P_2}{P_1}\right)$$

ΔG **is a state function, so we can** **propose a path** **from reactants to products and, as long as we start and end in the right places, we will get the correct value for** ΔG

Reactants → Products

Step 1 ΔG_1

Step 2 ΔG_2

Step 3 ΔG_3

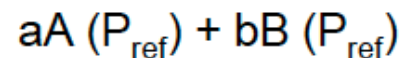Step 4 ΔG_4

$$\Delta G = \sum_{i=1}^{4} \Delta G_i$$
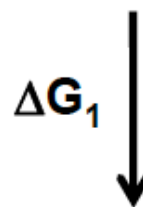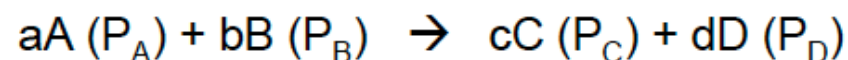
If four steps are involved, etc.

Choose *reference pressure* to be 1 atm.

Equilibrium and ΔG^o

For the <u>gas phase</u> reaction aA + bB $\Leftrightarrow$ cC + dD

$$\Delta G = -T\Delta S = nRT \ln\left(\frac{P_2}{P_1}\right)$$

aA (P_A) + bB (P_B) $\rightarrow$ cC (P_C) + dD (P_D)

ΔG_1 $\downarrow$

aA (P_{ref}) + bB (P_{ref})

propose a path

Let's say we start out at some **Pressure ($\neq$ 1 atm)**

Then, step 1: **Adjust P of reactants from $P_{initial}$ to P = 1 atm**
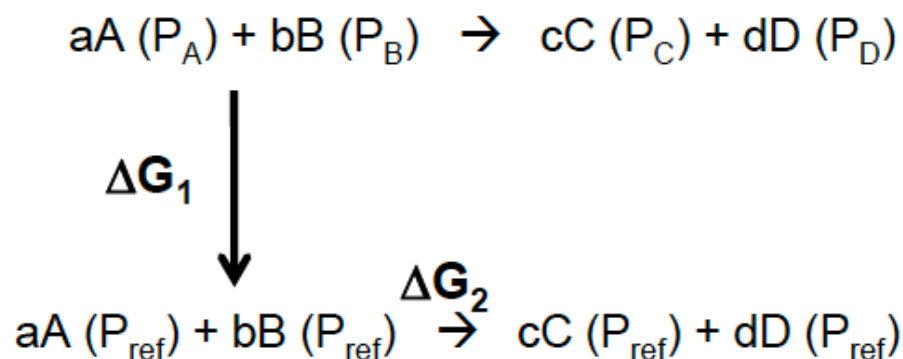
Choose T to be 298 K

We will have to account for this step (ΔG_1).

Equilibrium and ΔG^o

For the <u style="color:red">gas phase</u> reaction aA + bB $\Leftrightarrow$ cC + dD

$$\Delta G = -T\Delta S = nRT \ln\left(\frac{P_2}{P_1}\right)$$

aA (P_A) + bB (P_B) $\rightarrow$ cC (P_C) + dD (P_D)

ΔG_1 $\downarrow$

ΔG_2

aA (P_{ref}) + bB (P_{ref}) $\rightarrow$ cC (P_{ref}) + dD (P_{ref})

propose a path

Then, step 2: **Carry out reaction under standard conditions**

Use ΔG^o, ΔH^o, ΔS^o, etc. from tables
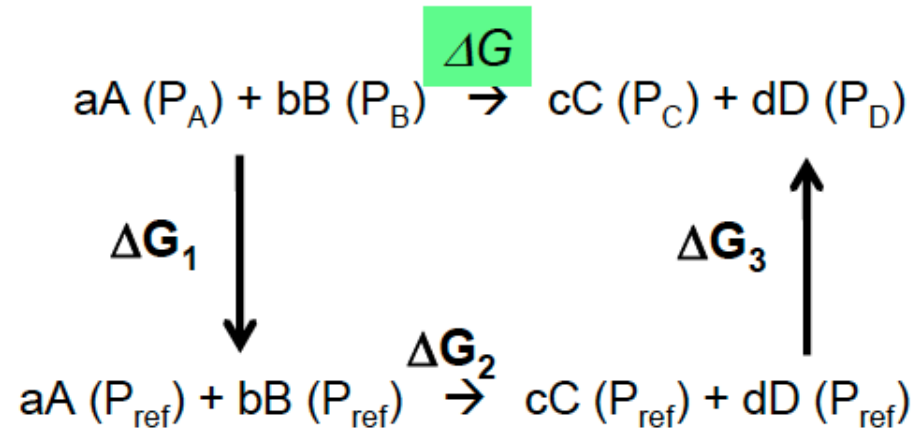
(25° C, 1 atm for gases, 1 M for solutions, see activity discussion on pp. 584-587 OGC for pure solids and liquids.)

Equilibrium and ΔG^o

For the <u>gas phase</u> reaction aA + bB $\Leftrightarrow$ cC + dD

$$\Delta G = -T\Delta S = nRT\ln\left(\frac{P_2}{P_1}\right)$$

$$\Delta G$$
$$aA\ (P_A) + bB\ (P_B) \rightarrow cC\ (P_C) + dD\ (P_D)$$

$\Delta G_1 \downarrow \qquad\qquad \Delta G_3 \uparrow$

$$\Delta G_2$$
$$aA\ (P_{ref}) + bB\ (P_{ref}) \rightarrow cC\ (P_{ref}) + dD\ (P_{ref})$$

propose a path

Then, step 3: **Adjust P of reactants from P=1 atm to $P_{products}$**

$$\Delta G = \sum_{i=1}^{3} \Delta G_i$$

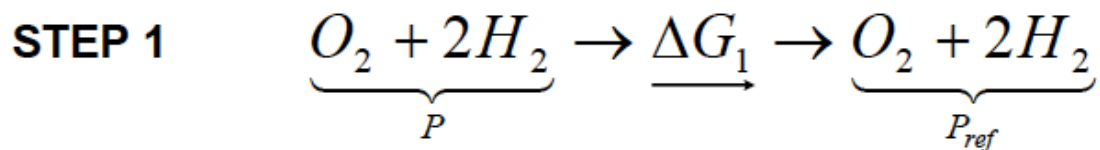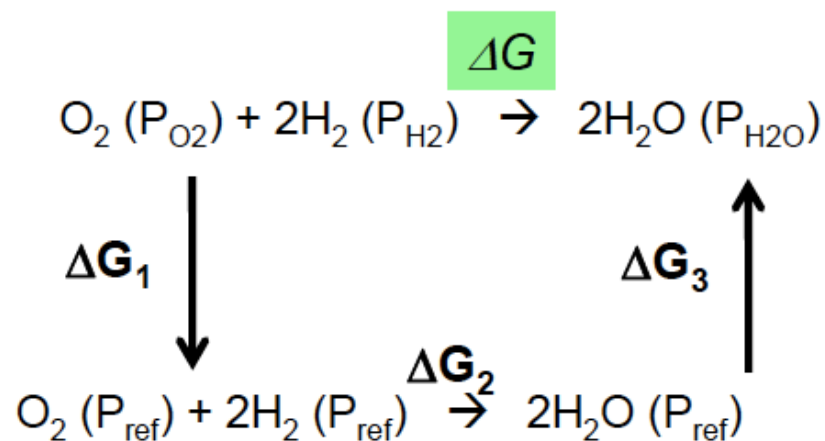# Equilibrium and ΔG^o Explicit Example

For the <u>gas phase</u> reaction $O_2 + 2H_2 \Leftrightarrow 2H_2O$

$$\Delta G = -T\Delta S = nRT\ln\left(\frac{P_2}{P_1}\right)$$

ΔG

$$O_2 (P_{O2}) + 2H_2 (P_{H2}) \rightarrow 2H_2O (P_{H2O})$$

$\Delta G_1 \downarrow \qquad\qquad\qquad \Delta G_3 \uparrow$

ΔG_2

$$O_2 (P_{ref}) + 2H_2 (P_{ref}) \rightarrow 2H_2O (P_{ref})$$

propose a path

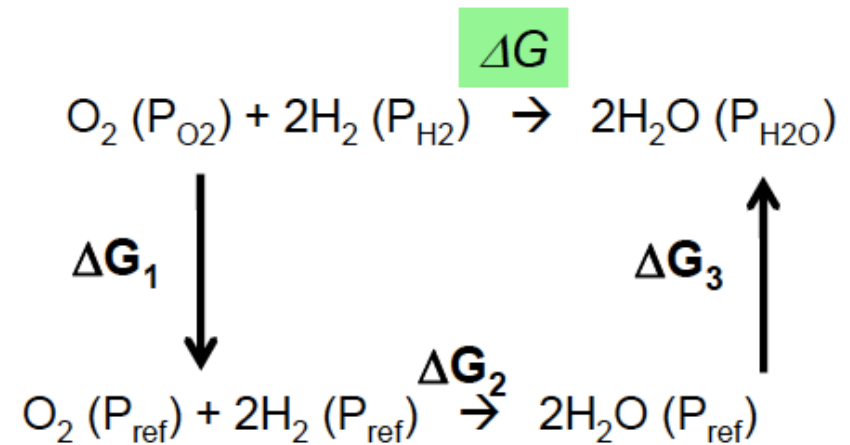**STEP 1** $$\underbrace{O_2 + 2H_2}_{P} \rightarrow \underline{\Delta G_1} \rightarrow \underbrace{O_2 + 2H_2}_{P_{ref}}$$

$$\Delta G_1 = RT\ln\left(\frac{P_{ref}}{P_{O_2}}\right) + 2RT\ln\left(\frac{P_{ref}}{P_{H_2}}\right) = RT\ln\left(\frac{P_{ref}}{P_{O_2}}\right) + RT\ln\left(\frac{P_{ref}}{P_{H_2}}\right)^2$$

Equilibrium and ΔG^o — Explicit Example

For the gas phase reaction $O_2 + 2\,H_2 \Leftrightarrow 2\,H_2O$

$$\Delta G = -T\Delta S = nRT \ln\left(\frac{P_2}{P_1}\right)$$

ΔG

$$O_2\,(P_{O2}) + 2H_2\,(P_{H2}) \rightarrow 2H_2O\,(P_{H2O})$$

$\Delta G_1 \downarrow$ $\Delta G_3 \uparrow$

$$O_2\,(P_{ref}) + 2H_2\,(P_{ref}) \xrightarrow{\Delta G_2} 2H_2O\,(P_{ref})$$

propose a path

STEP 2 **Carry out $O_2 + 2\,H_2 \Leftrightarrow 2\,H_2O$ under standard conditions**

$$\Delta G_2 = \sum_i \Delta G^0_{prod} - \sum_k \Delta G^0_{react}$$

Equilibrium and ΔG^o — Explicit Example

For the <u>gas phase</u> reaction $O_2 + 2H_2 \Leftrightarrow 2H_2O$

$$\Delta G = -T\Delta S = nRT \ln\left(\frac{P_2}{P_1}\right)$$

ΔG

$$O_2\,(P_{O2}) + 2H_2\,(P_{H2}) \;\rightarrow\; 2H_2O\,(P_{H2O})$$

$\Delta G_1 \downarrow \qquad\qquad\qquad\qquad \uparrow \Delta G_3$

$$O_2\,(P_{ref}) + 2H_2\,(P_{ref}) \overset{\Delta G_2}{\rightarrow} 2H_2O\,(P_{ref})$$

propose a path

STEP 3

$$\underbrace{2H_2O}_{P_{ref}} \rightarrow \underrightarrow{\Delta G_3} \rightarrow \underbrace{2H_2O}_{P}$$
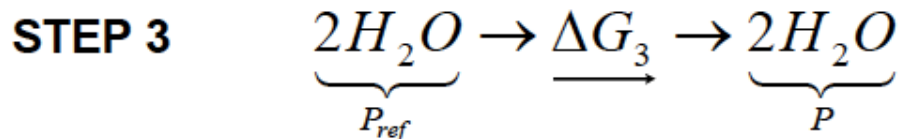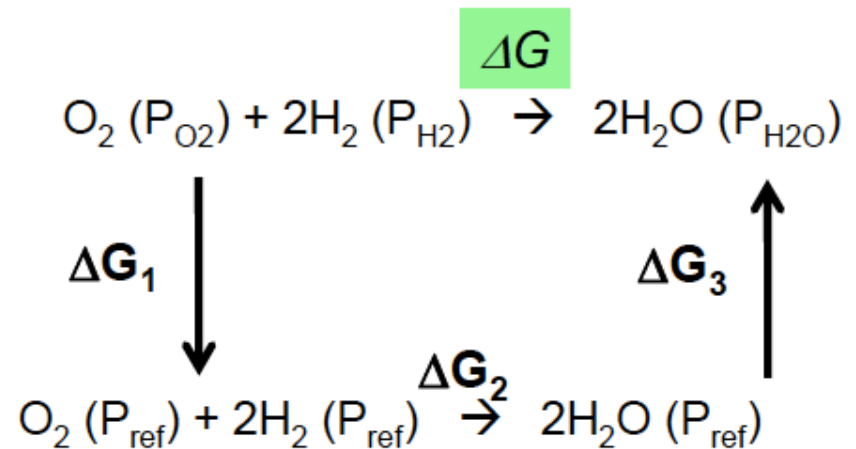
$$\Delta G_3 = 2RT \ln\left(\frac{P_{H_2O}}{P_{ref}}\right) = RT \ln\left(\frac{P_{H_2O}}{P_{ref}}\right)^2$$

Equilibrium and ΔG^o Explicit Example

$$\Delta G = \Delta G^o + \Delta G_{step1} + \Delta G_{step3}$$

$$\Delta G_1 = RT \ln\left(\frac{P_{ref}}{P_{O_2}}\right) + RT \ln\left(\frac{P_{ref}}{P_{H_2}}\right)^2$$

$$\Delta G_3 = 2RT \ln\left(\frac{P_{H_2O}}{P_{ref}}\right) = RT \ln\left(\frac{P_{H_2O}}{P_{ref}}\right)^2$$

$$\Delta G_{steps1\&3} = RT \ln\left(\frac{\left(\frac{P_{H_2O}}{P_{ref}}\right)^2}{\left(\frac{P_{H_2}}{P_{ref}}\right)^2\left(\frac{P_{O_2}}{P_{ref}}\right)}\right)$$

At equilibrium $\Delta G=0$

So, $\Delta G^o = -\Delta G_{steps1\&3}$

Equilibrium and ΔG^o

Explicit Example

This implies that:

$$-\Delta G^o = RT \ln \left(\frac{\left(\dfrac{P_{H_2O}}{P_{ref}} \right)^2}{\left(\dfrac{P_{H_2}}{P_{ref}} \right)^2 \left(\dfrac{P_{O_2}}{P_{ref}} \right)} \right)$$

Note that this looks a lot like the expression for K_P

$$K_P = \frac{[P_C]_{eq}^c [P_D]_{eq}^d}{[P_A]_{eq}^a [P_B]_{eq}^b}$$

Except this expression is unit-less

Equilibrium and ΔG^o Explicit Example

When we are away from equilibrium

$$\Delta G = \Delta G^o + RT \ln \left(\frac{\left(\dfrac{P_{H_2O}}{P_{ref}} \right)^2}{\left(\dfrac{P_{H_2}}{P_{ref}} \right)^2 \left(\dfrac{P_{O_2}}{P_{ref}} \right)} \right)$$

From standard states

Accounts for the actual conditions on the reaction (for gases), with $P_{ref} = 1$ atm

If $\Delta G < 0$ reaction proceeds spontaneously
If $\Delta G > 0$ reaction proceeds in reverse spontaneously
If $\Delta G = 0$ reactants and products are at equilibrium

Equilibrium and ΔG^o Calculation

P H_2O = 0.1 atm

P O_2 = 1 atm

P H_2 = 0.05 atm

T = 298K; V=1liter

Substance	ΔH_f^o (kJ·mol^{-1})	S^o (J·K^{-1}·mol^{-1})	ΔG_f^o (kJ·mol^{-1})
H_2	0	130.57	-TΔS^o
O_2	0	205.03	-TΔS^o
H_2O (gas)	-241.82	188.72	-228.59

$\Delta H^o_{rxtn} = \Delta H_{products} - \Delta H_{reactants}$ = -241.82 kJ·mol^{-1}

$T\Delta S_{rxtn} = TS_{products} - TS_{reactants}$ = 298K (188.72 – 0.5(205.03)- 130.57) = -13.1 kJ·mol^{-1}

$\Delta G^o_{rxtn}=\Delta H-T\Delta S$= -241.82 - (-13.1) = -228.7 kJ·mol^{-1}

$$\Delta G = \Delta G^o + RT \ln \left(\frac{\left(\frac{P_{H_2O}}{P_{ref}} \right)^2}{\left(\frac{P_{H_2}}{P_{ref}} \right)^2 \left(\frac{P_{O_2}}{P_{ref}} \right)} \right)$$

= -228.7 kJ mol^{-1}

+ 8.314 J mol^{-1} K^{-1} (298 K) ln[(0.1)^2(0.05) $^{-2}$(1)]

= - 225 kJ mol^{-1}

Reaction proceeds with a vengeance!

Equilibrium and ΔG^o

P H_2O = 0.1 atm

P O_2 = 1 atm

P H_2 = ? ? ?

  T = 298K; V=1liter

Substance	ΔH_f^o (kJ·mol^{-1})	S^o (J·K^{-1}·mol^{-1})	ΔG_f^o (kJ·mol^{-1})
H_2	0	130.57	-TΔS^o
O_2	0	205.03	-TΔS^o
H_2O (gas)	-241.82	188.72	-228.59

Suggested thought exercise #1:

At what pressure of H_2 will the system be in equilibrium?

 Suggested thought exercise #2:

Example #2:   Consider the reaction   BrNO(g) ⇔ NO(g) + ½ Br_2(g)

If we mix the following quantities at 298K, will we get a spontaneous reaction and, if so, in what direction?

Pressure BrNO = 0.8 atm   Pressure NO = 0.1 atm   Pressure Br_2 = 0.16 atm

Equilibrium and ΔG^o

What happens if the system is perturbed?

Le Chatelier's Principle:
When stress is applied to a system at equilibrium, the system will respond so as to relieve this stress.

- Concentration changes
- Temperature changes
- Pressure changes
- Addition of a catalyst
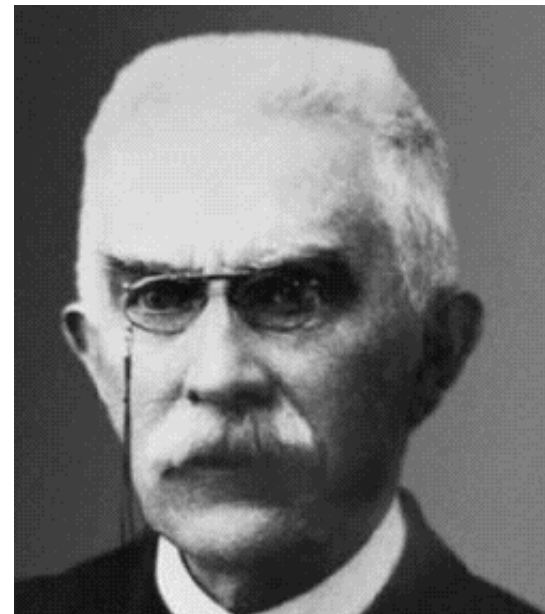
Can compare the reaction quotient, Q, to K in order to determine the direction of change (Section 14.6, OGC).

# Equilibrium and ΔG^o

$$-\Delta G^0 = RT \ln K_{eq}$$

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

**Depending on the sign & magnitude of ΔS, ΔG can:**
- may go from + to – valued w/ increasing T
- may go from – to + valued w/ increasing T
- may decrease in magnitude
- may increase in magnitude
- may remain unchanged

For many systems, ΔG is relatively invariant to at least small T changes (i.e. the entropic contributions to ΔG are often relatively small)
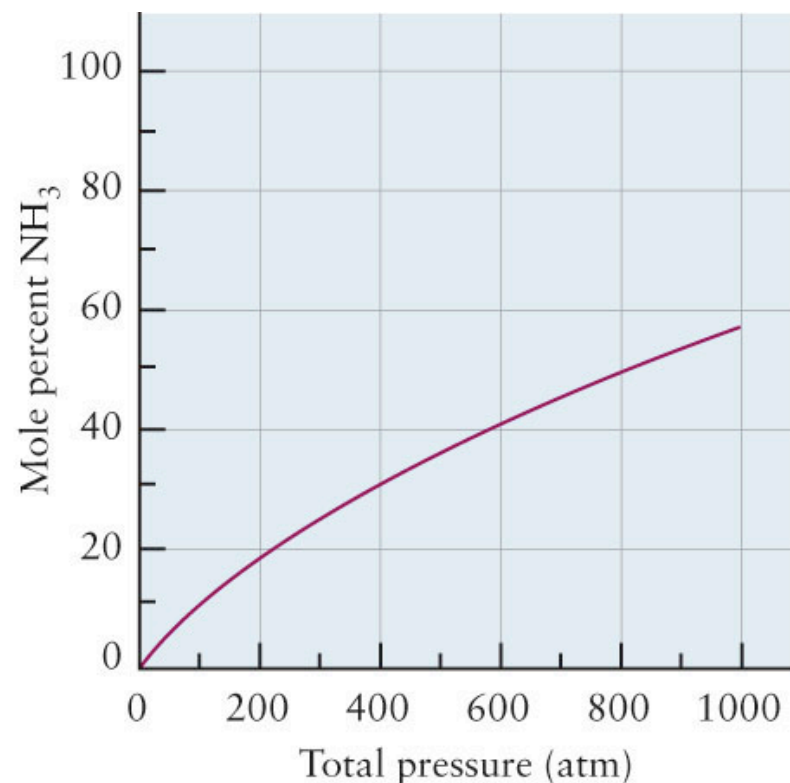
Le Chatelier's Principle

N_2 + 3 H_2 (g) $\longrightarrow$ 2 NH_3 (g)   ΔG = -33.32 kJ
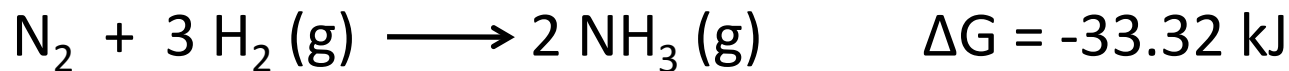
(Haber process, consumes several percent of the world's natural gas production, to make the H_2):
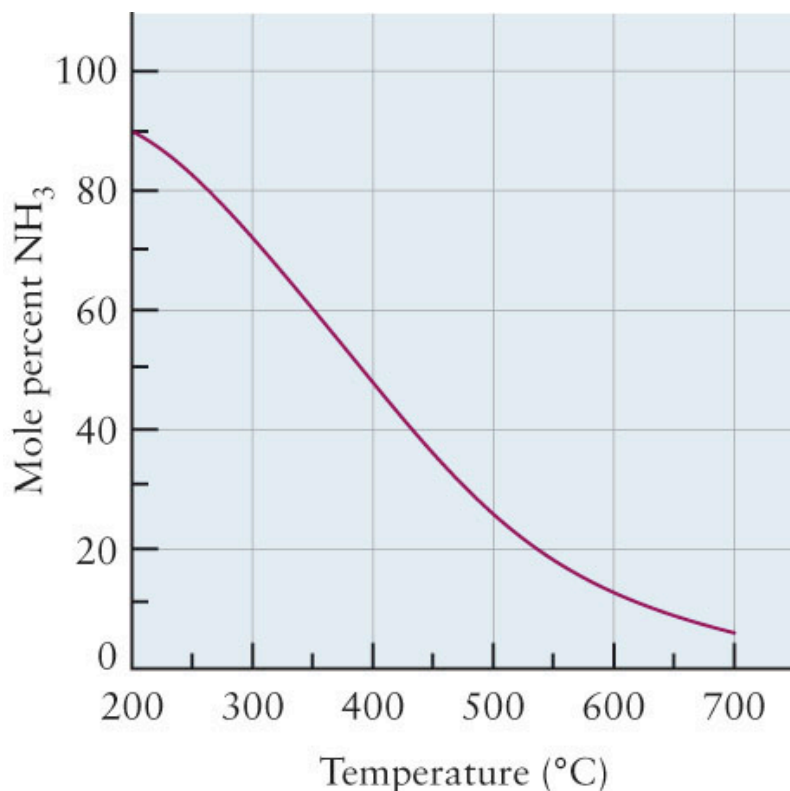
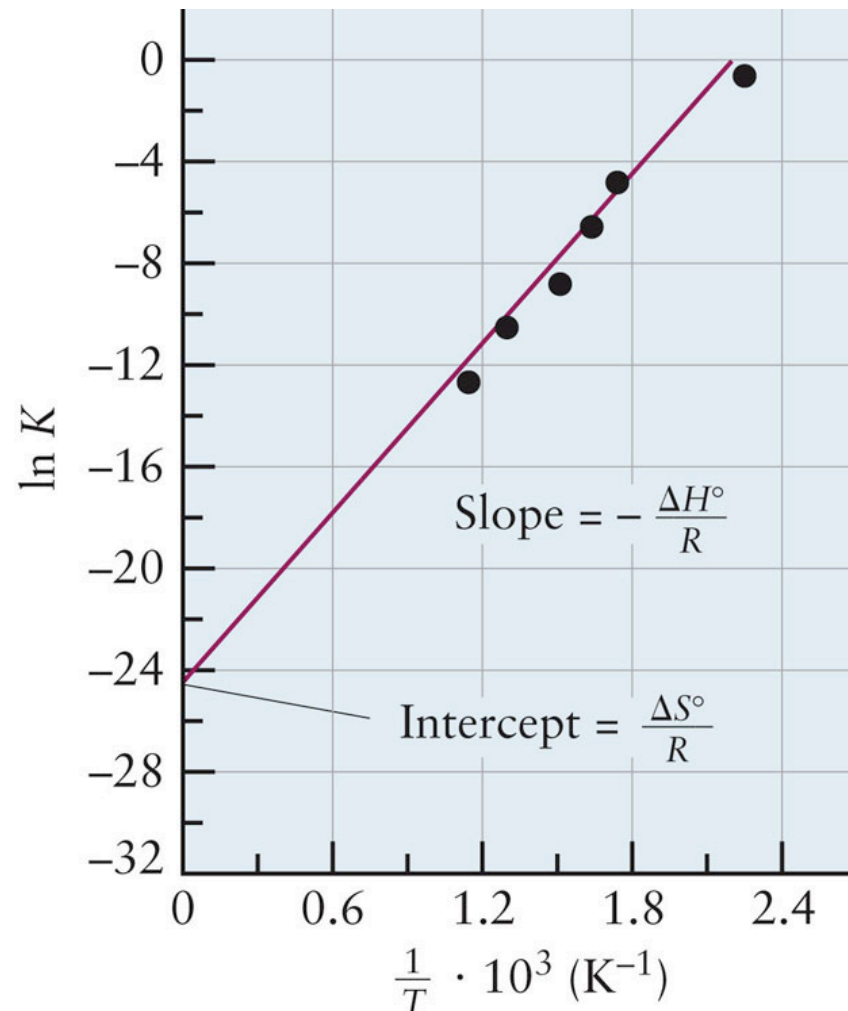Exothermic   4 moles to 2

Le Chatelier's Principle

$$\ln K = -\Delta G^o/RT = -\Delta H^o/RT + \Delta S^o/R$$

Can thus use the dependence of K with temperature to measure the enthalpy and entropy components. Important in atmospheric chemistry, esp. O_3 formation.
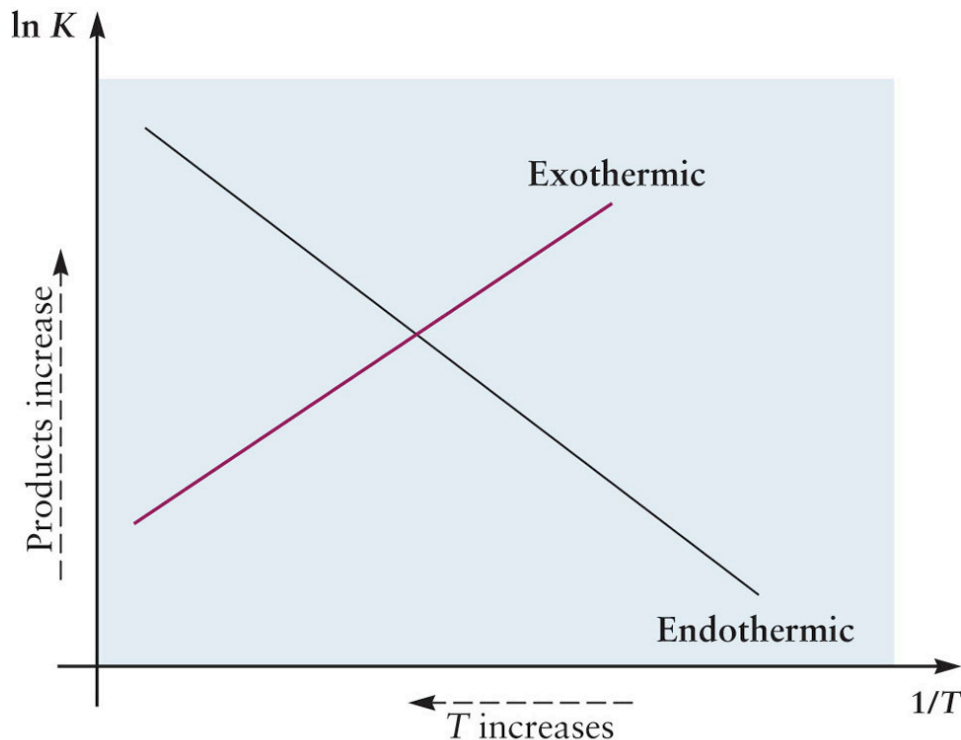

$$\ln (K_2/K_1) = -\Delta H^o[1/T_2 - 1/T_1]/R$$

(the van't Hoff equation)
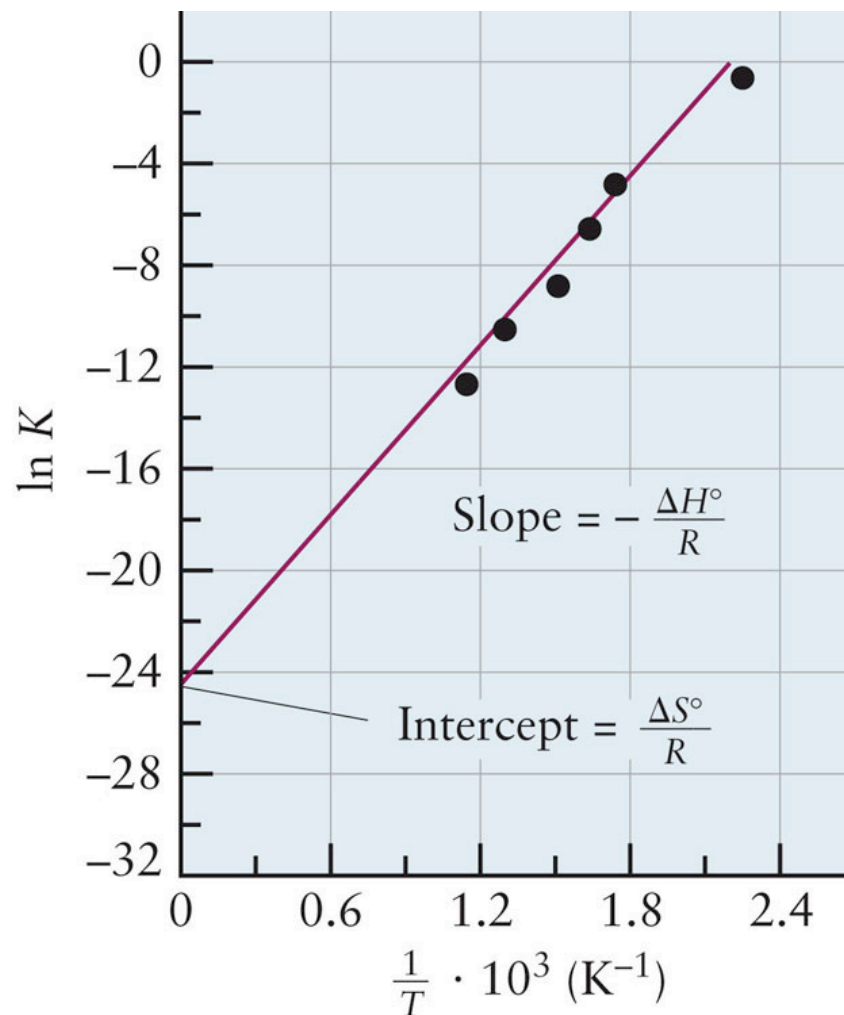

Slope $= -\dfrac{\Delta H^\circ}{R}$

Intercept $= \dfrac{\Delta S^\circ}{R}$

$\ln K$

$\dfrac{1}{T} \cdot 10^3 \ (K^{-1})$

© 2007 Thomson Higher Education

Le Chatelier's Principle

$$\ln K = -\Delta G^o/RT = -\Delta H^o/RT + \Delta S^o/R$$
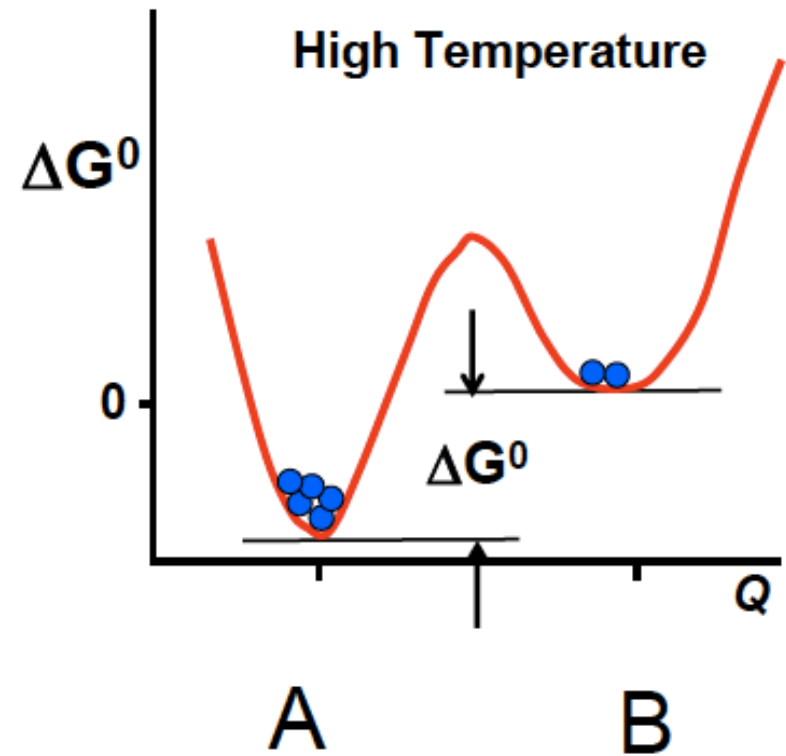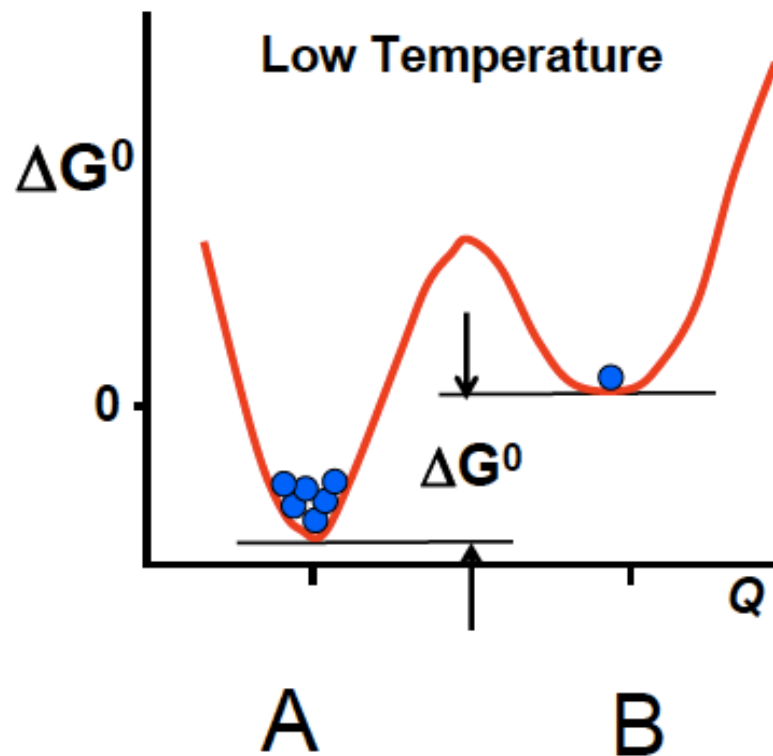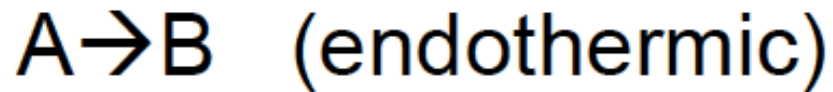

© 2007 Thomson Higher Education

Can we rationalize the temperature dependence physically, and not rely solely on the equations?

© 2007 Thomson Higher Education

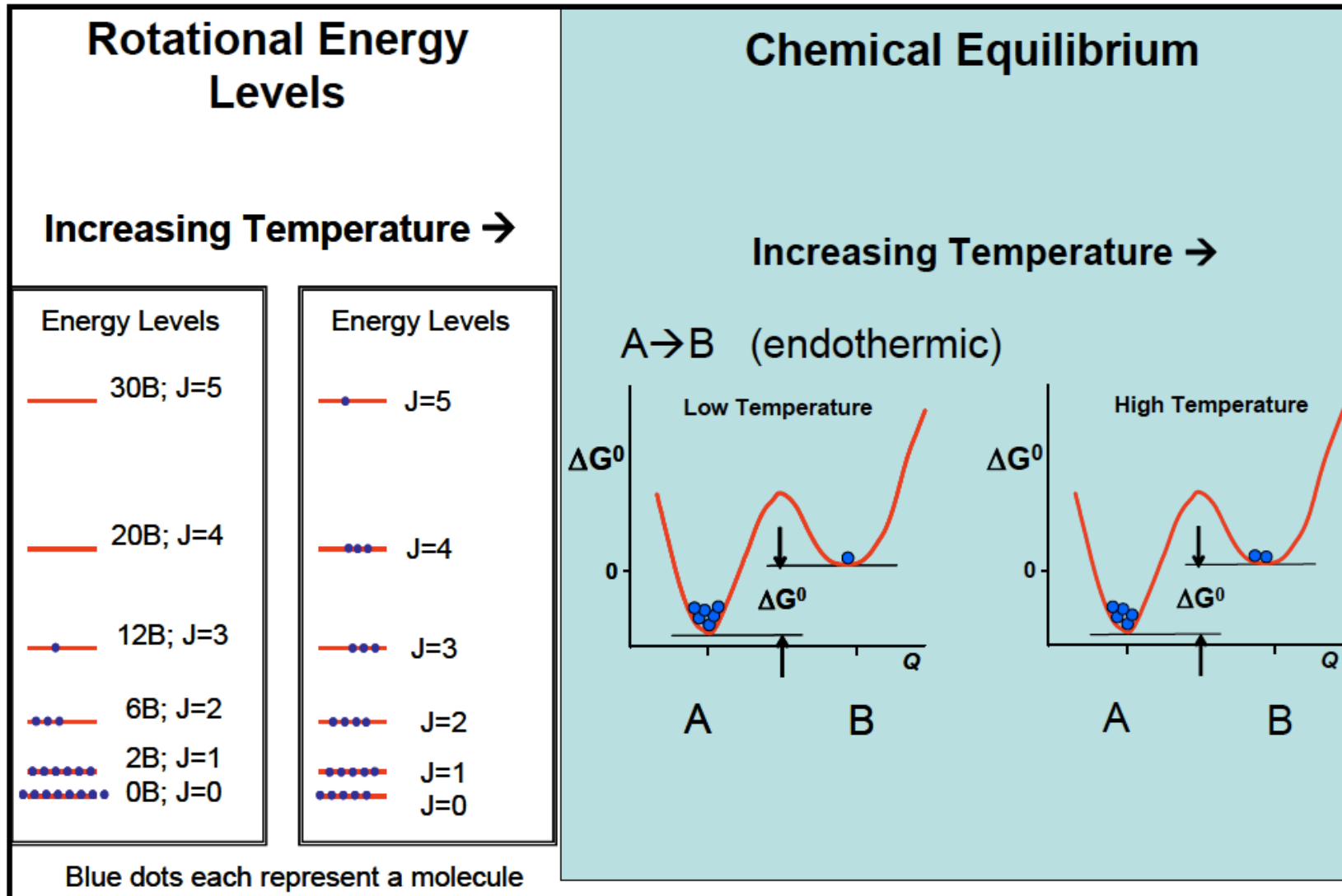# Le Chatelier's Principle

Ties to Boltzmann:

$A \rightarrow B$ (endothermic)

As Temperature increases, the population of B increases relative to A

Le Chatelier's Principle

Ties to Boltzmann:

Rotational Energy Levels

Increasing Temperature →

Energy Levels	
30B; J=5	
20B; J=4	
12B; J=3	
6B; J=2	
2B; J=1	
0B; J=0	

Energy Levels	
J=5	
J=4	
J=3	
J=2	
J=1	
J=0	

Blue dots each represent a molecule

Chemical Equilibrium

Increasing Temperature →

$A \rightarrow B$ (endothermic)

Low Temperature

ΔG^0

ΔG^0

A   B

High Temperature

ΔG^0

ΔG^0

A   B

Le Chatelier's Principle

Ties to Boltzmann:

Rotational Energy Levels

Endothermic reaction

$$E_J = J(J+1)B_{LiF}$$

E

ΔG ≈ ΔE
(exactly true at
a given T)

aA ⇔ bB
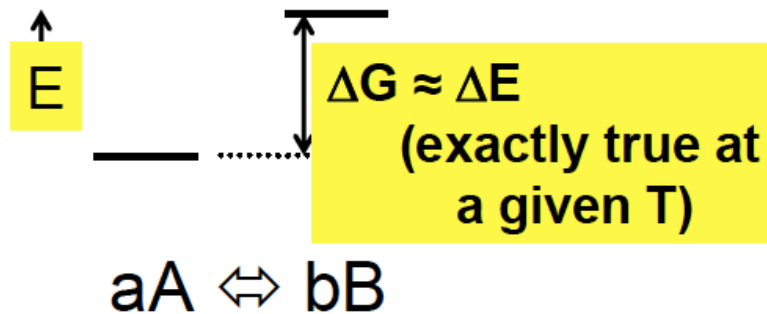
$$-\Delta G^0 = RT \ln K_{eq}$$

$$\frac{-\Delta G^0}{RT} = \ln K_{eq}$$

$$\frac{n'}{n''} = \frac{g'}{g''} e^{\frac{-\Delta E}{k_B T}}$$

$$e^{\frac{-\Delta G^0}{RT}} = K_{eq} = \frac{[B]^b}{[A]^a}$$

Energy Levels
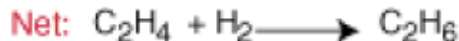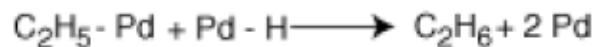
30B

20B

12B

6B

2B
0B

Le Chatelier's Principle

Chemical catalysts accelerate reactions but do not the equilibrium, since they act principally on E_a.
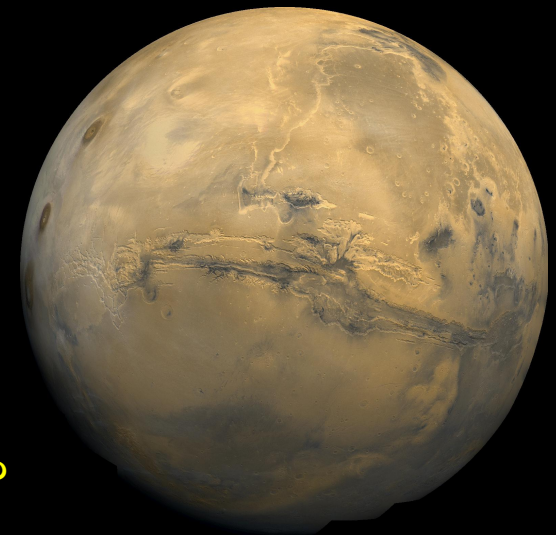

Uncatalyzed mechanism:

$$H_2 \rightleftharpoons 2\,H$$
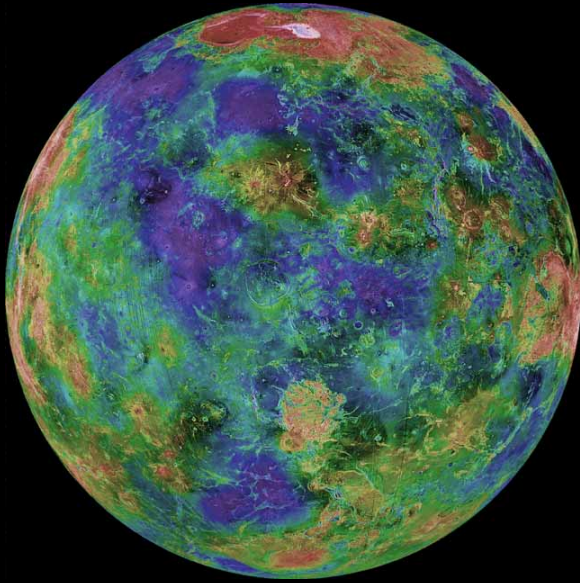
$$C_2H_4 + H \longrightarrow C_2H_5$$

$$C_2H_5 + H \longrightarrow C_2H_6$$

Net: $C_2H_4 + H_2 \longrightarrow C_2H_6$

Pd catalyzed mechanism

$$H_2 + 2\,Pd \rightleftharpoons 2\,Pd\text{-}H$$

$$C_2H_4 + Pd\text{-}H \longrightarrow C_2H_5\text{-}Pd$$

$$C_2H_5\text{-}Pd + Pd\text{-}H \longrightarrow C_2H_6 + 2\,Pd$$

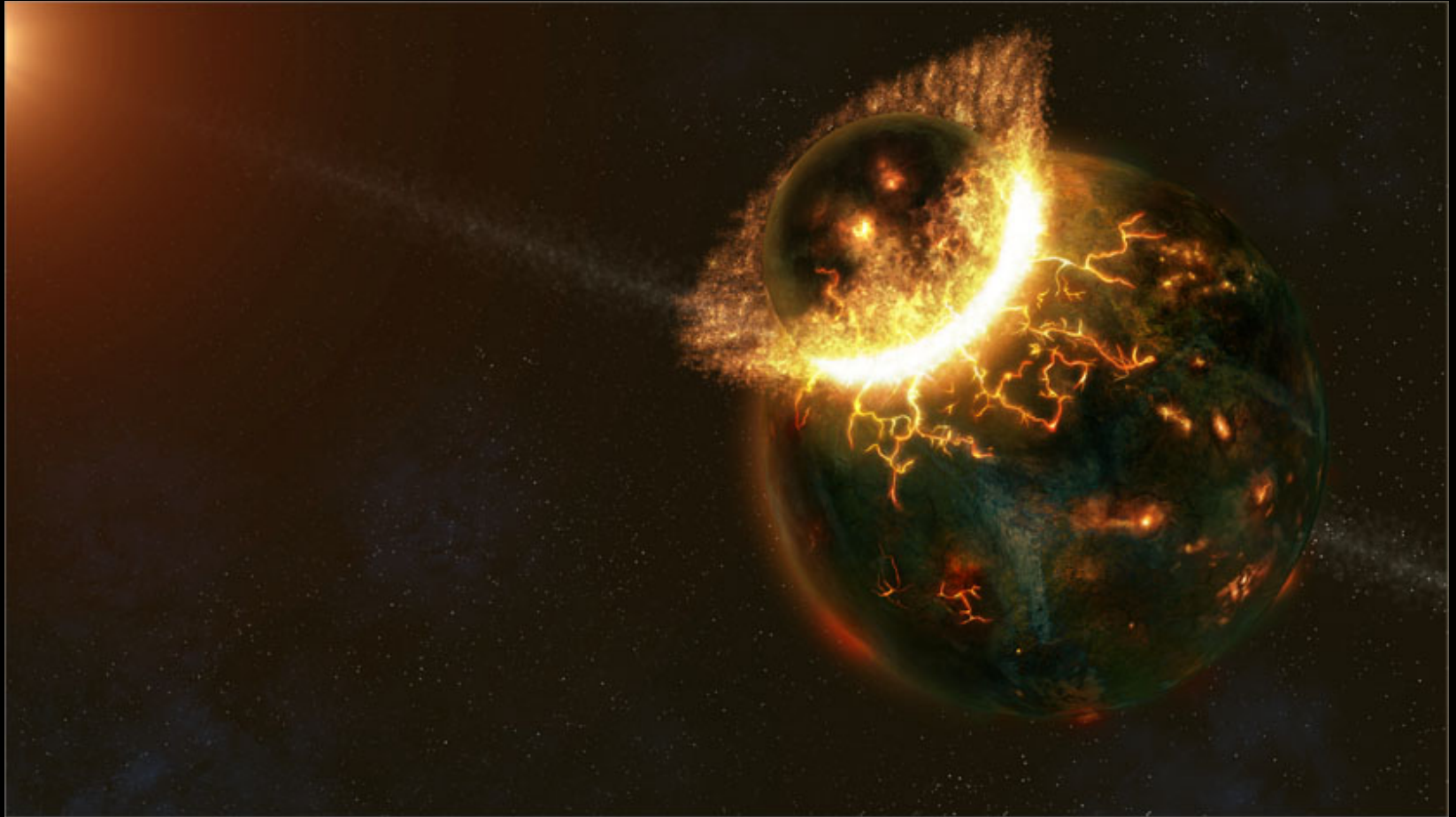Net: $C_2H_4 + H_2 \longrightarrow C_2H_6$
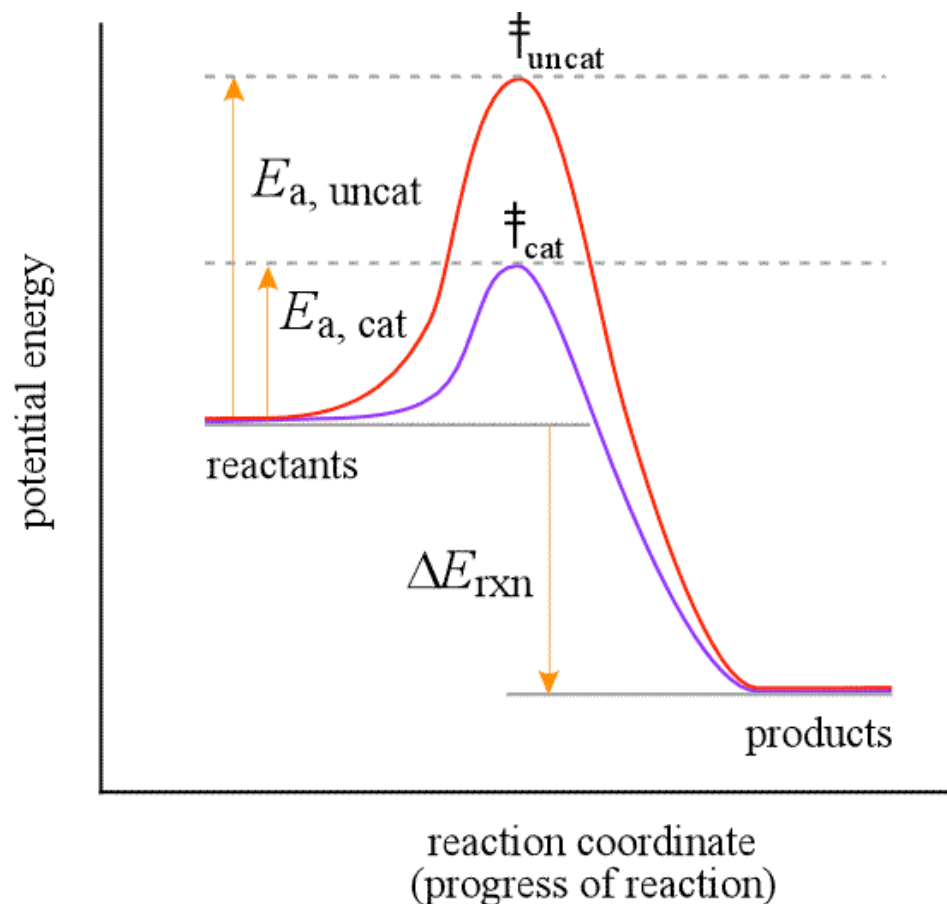
Chemistry in Context: Building a habitable planet, or

From whence water and organics?

And, why is the D/H ratio in the oceans $10x$ that in Jupiter?

Why should we consider volatiles from the outer solar system as the source of terrestrial water?

"Earth 4.5 AE B.C. – Fishing is extremely poor, especially in August."

Cliff Hauptman, *The Complete History of Fishing*

Impacts!