

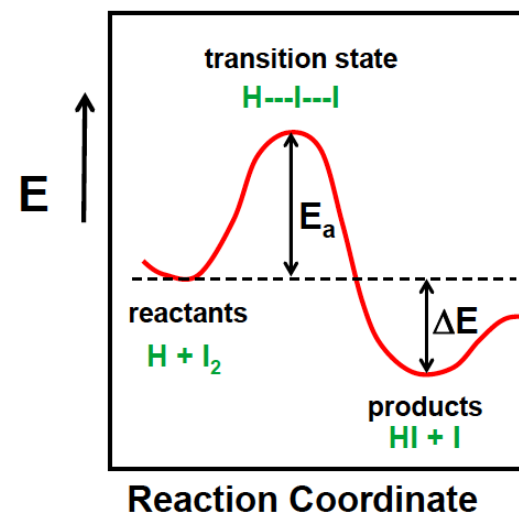
Ch 1b Lecture 15

February 11th, 2013

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

Today: Spontaneous Process & Equilibrium, Part I

Reading: OGC Chapter 13, Section 13.7,
Chapter 14, Sections 14.1-14.3



Last time: The Historical Motivation of Entropy & the 2nd Law

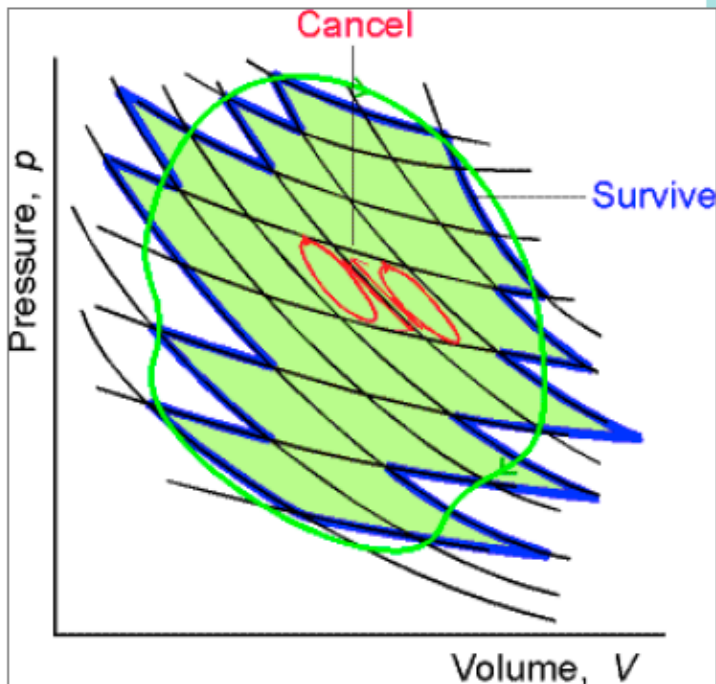
$$\frac{q_f}{T_h} + \frac{q_b}{T_l} = 0$$

No matter how we traverse this loop, this equation holds. Thus:

The implication is that q/T is a state function

f denotes forward pathway $A \rightarrow B \rightarrow C$

b denotes return pathway $C \rightarrow D \rightarrow A$



More generally, Clausius defined entropy as:

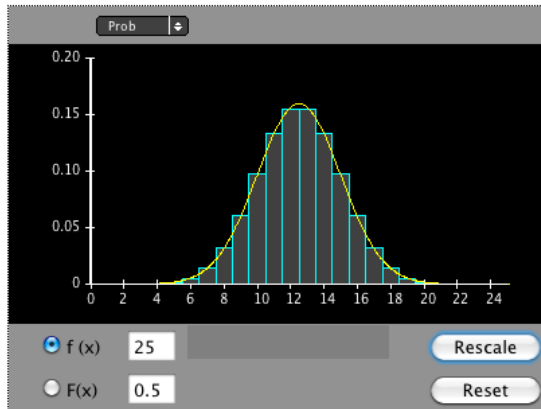
$$\Delta S \equiv \int_i^f \frac{dq_{rev}}{T}$$

Units $J \cdot K^{-1}$

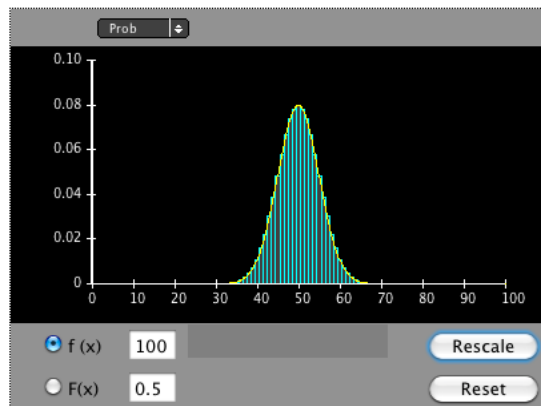
'i , f' here mean initial and final

$$\Delta S = \oint_{\text{perimeter}} \frac{dq_{rev}}{T} = 0$$

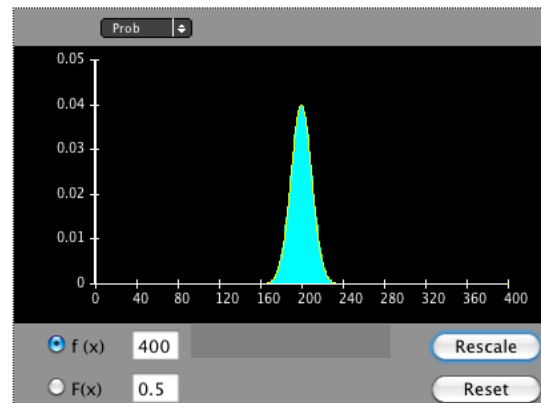
A microscopic approach to Entropy



As the number of trials increases, both the mean and the dispersion go up...



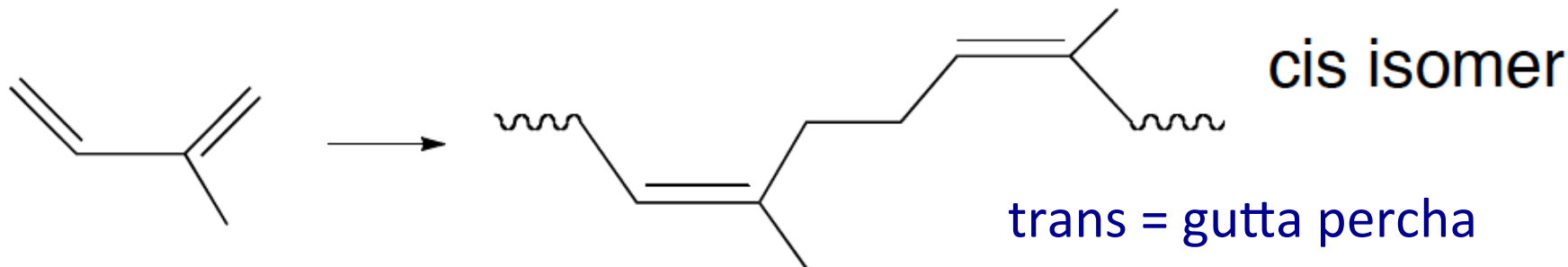
But the width of the distribution *relative* to the mean decreases...



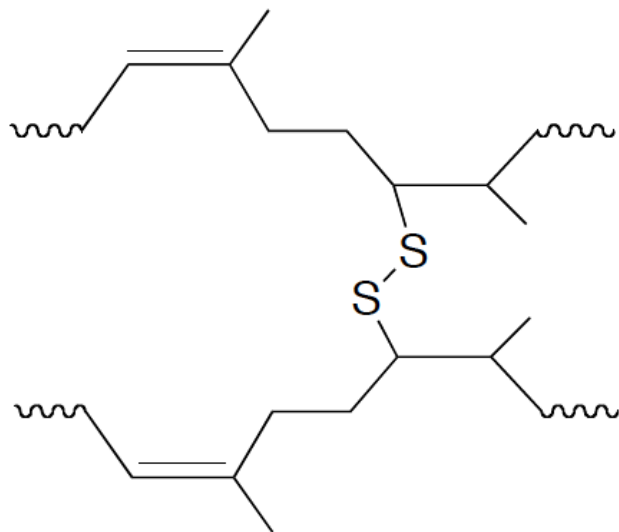
Thus, for ensembles of order N_A , fluctuations that measurably depart from the most likely outcome are insignificant!

Entropy & Polymers

Rubber $[(C_5H_8)_n]$, Michael Faraday 1826] is polymerized isoprene:



The degree of polymerization is ~ 5000 in natural rubber.



Vulcanization (Goodyear, 1839)
introduces sulfur cross-links.
Typical spacing ~ 100 isoprene units.

Especially in environments such as
Los Angeles, rubber is susceptible to
oxidation & aging.

Question: Why do rubber bands *shrink* when heated?

Entropy & Polymers – Kelvin (1857)/Joule (1859)

Treat in one dimension, assume Hooke's law when stretched by x :

$$\text{Force} = f = kx \quad \& \quad dU = dq + dw = TdS + fx \quad (\text{no PdV work})$$

Experimentally, for small x a rubber band is nearly ideal, so at fixed T :

$$dU = dq + dw \approx 0 \quad \& \quad dq = TdS = -fx$$

When a rubber band is stretched, $x > 0$, and the force constant is positive. Thus, stretching is **exothermic**, and is accompanied by a *decrease* in entropy.

Can we make sense of this at the molecular level, and estimate the force constant from fundamentals?

Entropy & Polymers – Rubber Elasticity & the Random Walk Problem

Basic idea:

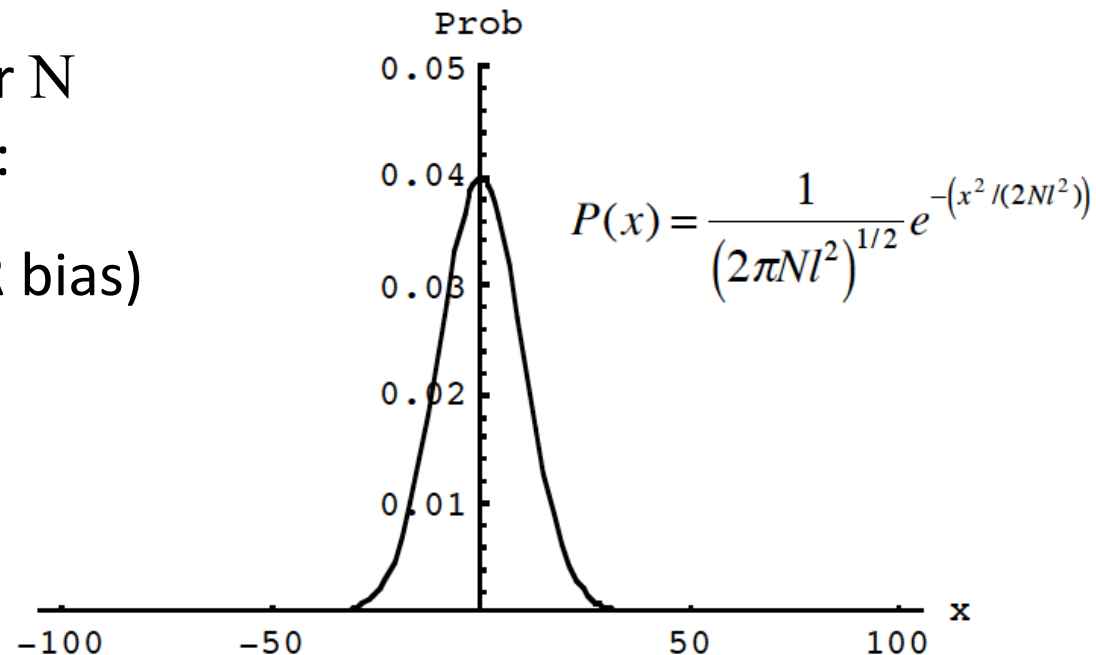
Model the polymer as a 1-D random walk problem, with $N_R + N_L = N$ total steps (N_R = steps to the right, etc.) of length l . Thus, the end-to-end length is just $(N_R - N_L)l = nl$.

The average and mean square displacement after N steps can be shown to be:

$$\langle x(N) \rangle = 0 \quad (\text{no L/R bias})$$

$$\langle x^2(N) \rangle = \sigma^2 = Nl^2$$

For large N , this is our old friend the Gaussian distribution:



Entropy & Polymers – Rubber Elasticity & the Random Walk Problem

What next? Recall that $S = k_B \ln \Omega$

Here, $\Omega(x)$ is the number of ways for a chain of N steps (the total length is Nl) to have an end-to-end length x .

$\Omega(x)$ is the number of different chains (2^N) times the probability of forming a chain of end-to-end length x , or $\Omega(x) = 2^N P(x)$ (from slide #6). Based on this simple model, the entropy change in extending a chain from the origin to a conformation with an end-to-end length x is:

$$\Delta S = S(x) - S(0)$$

$$= k_B \ln \Omega(x) - k_B \ln \Omega(0) = k_B \ln \frac{\Omega(x)}{\Omega(0)} = -\frac{k_B}{2Nl^2} x^2$$

Entropy & Polymers – Rubber Elasticity & the Random Walk Problem

From our thermodynamic analysis, the restoring force can be related to S by:

$$f = -T \left(\frac{\partial S}{\partial x} \right)_{T,V}$$

Inserting into our random walk analysis yields:

$$S(x) = -\frac{k_B}{2Nl^2} x^2$$
$$\left(\frac{\partial S}{\partial x} \right)_{T,V} = -\frac{k_B}{Nl^2} x$$

Thus, force is indeed proportional to displacement (**Hooke's Law**), and

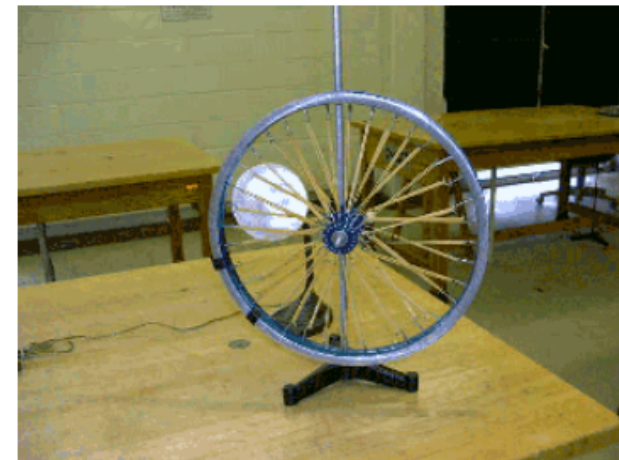
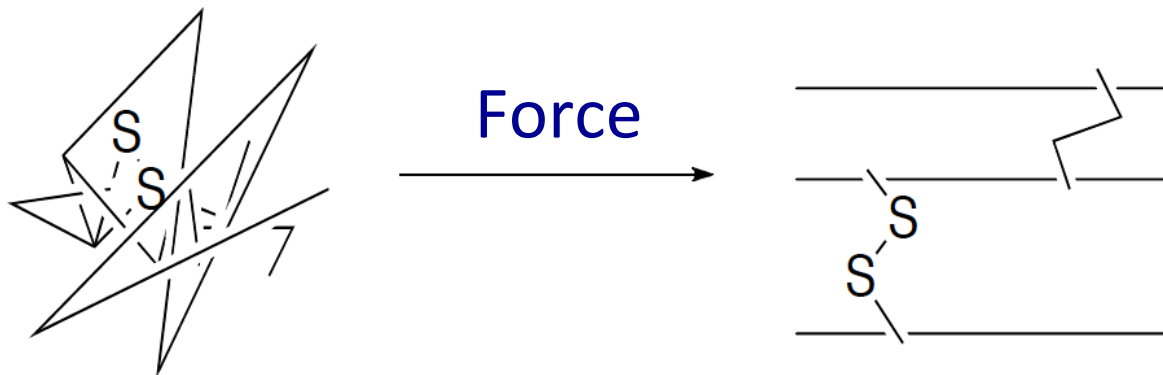
$$\text{force constant} = \frac{k_B T}{Nl^2}$$

Entropy & Polymers – Rubber Elasticity

Since $f \sim T$, the force needed to extend the chain by a certain amount increases with T , that is, the rubber band shrinks as it heats up. Bungee jumping at day/night?

$$f = -T \left(\frac{\partial S}{\partial x} \right)_{T,V} = \frac{k_B T}{N l^2} x$$

At the molecular level, we can understand this behavior in terms of the likely conformations of a long chain polymer containing freely rotating bonds, that is:



Entropy & Polymers – Rubber Elasticity

Elasticity is an example of a general phenomenon:

Disordered state \longleftrightarrow **Ordered State** + heat
[**Compact** \longleftrightarrow **Extended** + heat (for rubber)]

For a reversible process, $\Delta S = \Delta q/T$. Since $\Delta S < 0$ when the rubber band stretches, Δq is also < 0 , which corresponds to heat given off by the system (i.e. this is an exothermic process). True for rubber bands, protein unfolding, bilayer melting, phase transitions...

An ordered phase is stabilized at low temperature and the transition to the disordered phase is associated with heat uptake (the TdS term increasingly favors the disordered form with increasing temperature).

Entropy Overview:

In many cases, we will care about the possibilities that associated with chemical reactions taking place under constant pressure and temperature.

Reversible processes

$$\Delta S \text{ of system} + \text{surroundings} = 0$$

Irreversible processes

$$\Delta S \text{ of system} + \text{surroundings} > 0$$

A situation where

$$\Delta S \text{ of system} + \text{surroundings} < 0$$

Is not possible

This will lead us to consider a new state function, the Gibbs Free Energy, or G , defined as:

$$G = H - TS$$

Entropy Overview, Numerical Example

First for a reversible, non-isothermal process:

Reversible processes

ΔS of system + surroundings = 0

Example (ideal gas): $n = 2$; $V = 10$ Liters; $T = 300\text{K}$

For a reversible, isobaric compression to 5 Liters

ΔS_{gas} and $\Delta S_{\text{surrounding}} = ?$

$$\Delta P = 0$$

$$V_2/V_1 = 0.5$$

$$T_2/T_1 = 0.5$$

$$\text{So } T_2 = 150\text{K}$$

$$\Delta S_{\text{gas}} = \int_{T_1}^{T_2} dq_{\text{rev}} = nc_P \ln\left(\frac{T_2}{T_1}\right) = 2\left(\frac{5}{2} \cdot 8.314 \text{ J} \cdot \text{mol}^{-1} \text{K}^{-1}\right) \ln\left(\frac{150}{300}\right)$$

$$= -29 \text{ J K}^{-1}$$

$$\Delta S_{\text{surroundings}} = 29.1 \text{ J} \cdot \text{K}^{-1}$$

Entropy Overview, Numerical Example:

Take same system ($V_2 = 5$ liters; $T = 150$ K; $n=2$) and do a **reversible, isothermal** expansion back to 10 Liters

$$\Delta T = 0 \text{ so } q = -w$$

$$w = -nRT \int_{V_1}^{V_2} \frac{1}{V} dV = -nRT \ln \frac{V_2}{V_1} = -q$$

$$w = -1728 \text{ J}; q = 1728 \text{ J}$$

$$\Delta S_{\text{system}} = 1728 \text{ J} / 150 \text{ K} = 11.5 \text{ J K}^{-1}$$

$$\Delta S_{\text{surroundings}} = -11.5 \text{ J K}^{-1}$$

Entropy Overview, Numerical Example:

Continuing with the same system ($V_2 = 5$ liters; $T = 150$ K; $n=2$) and an **irreversible**, **isothermal** expansion back to 10 Liters

$$w = -P_{ext}\Delta V = -2.46(10L - 5L) = -12.3L \cdot atm = \sim -1230J$$

Since $\Delta T = 0$ so $q = -w = 1230$ J

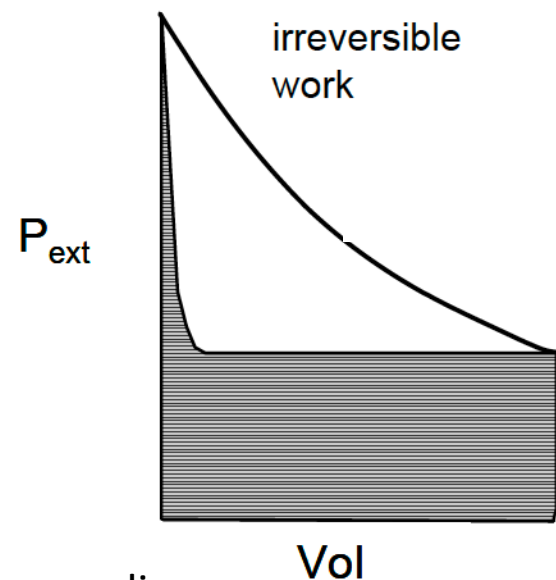
$$\Delta S_{system} = +11.5 \text{ J K}^{-1} \text{ still!!}$$

State function!!

$$\Delta S_{surroundings} = -1230J/150K = -8 \text{ J K}^{-1}$$

$$\begin{aligned} \Delta S_{total} &= 11.5 \text{ J K}^{-1} - 8 \text{ J K}^{-1} \\ &= 3.5 \text{ J K}^{-1} \end{aligned}$$

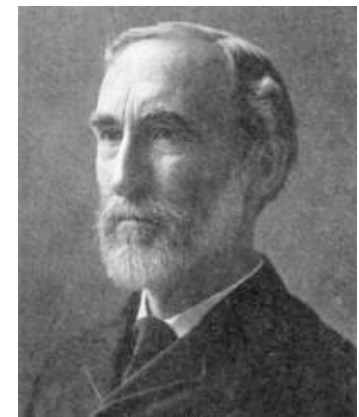
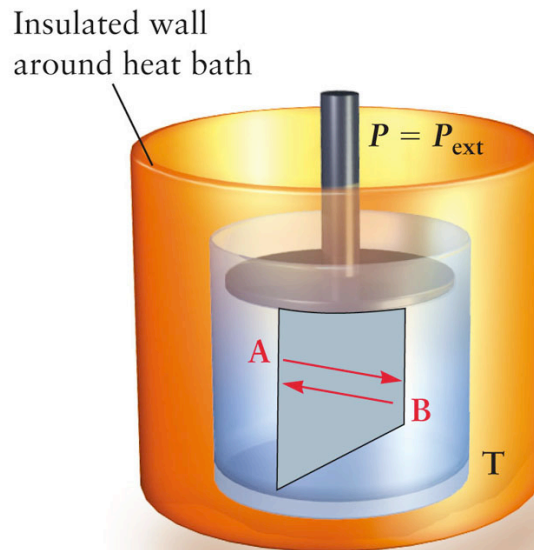
$$\Delta S_{total} > 0$$



It's tedious to have to keep track of both the system & the surroundings.
Wouldn't it be nice to just have to worry about the system?

The Gibbs Free Energy, or G

Imagine a system held at constant P , T of two components, initially held separately and then allowed to mix. The enthalpy ΔH determines the nature of the heat flow... Thus



No, not Leroy, J. Willard, Yale University.

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr}$$

and

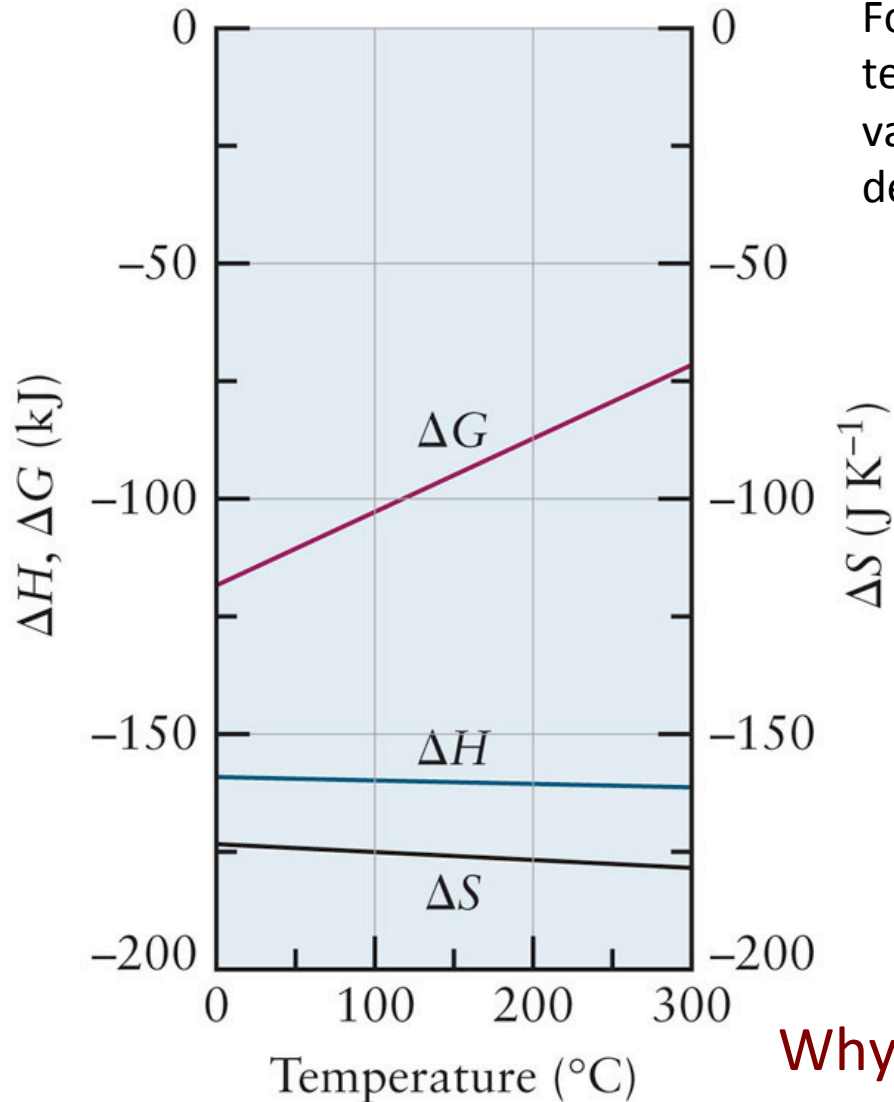
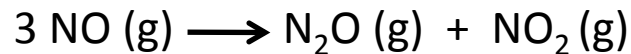
$$\Delta S_{surr} = -\Delta H_{sys}/T_{surr}$$

$$\Delta S_{total} = -(\Delta H_{sys} - T_{surr}\Delta S_{sys})/T_{surr} = \Delta(H_{sys} - TS_{sys})/T$$

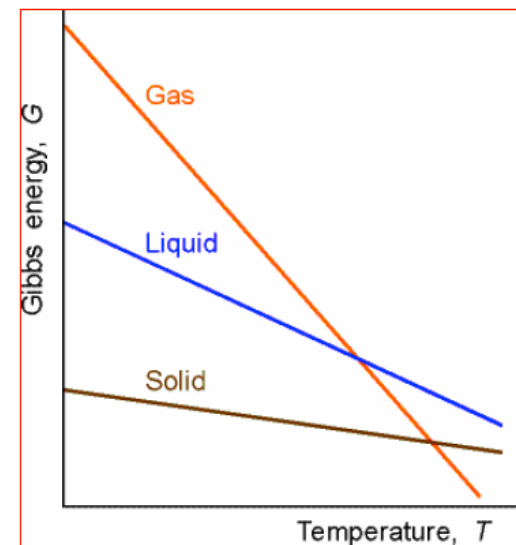
And if we define $G = H - TS$, then

$$\Delta S_{total} = -(\Delta G_{sys})/T \quad \text{and only the } \textit{system} \text{ need be examined.}$$

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



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



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

Why is $\Delta S < 0$?

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

The Gibbs Free Energy, or G

For chemical reactions at a constant temperature

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

G is the Gibbs Free Energy

$\Delta G_{\text{sys}} > 0$ Non-spontaneous process

$\Delta G_{\text{sys}} = 0$ Reversible process

$\Delta G_{\text{sys}} < 0$ Spontaneous process

The Gibbs Free Energy, or G

The ΔG° of a reaction at 25° can be determined using **Standard Free Energies of Formation**:

$$\Delta G^\circ = \sum n \Delta G_f^\circ(\text{products}) - \sum n \Delta G_f^\circ(\text{reactants})$$

What is ΔG° at 25°C for the reaction:



$$\begin{aligned}\Delta G^\circ &= 2 \Delta G_f^\circ(\text{NH}_3, \text{g}) - \Delta G_f^\circ(\text{N}_2, \text{g}) - 3 \Delta G_f^\circ(\text{H}_2, \text{g}) \\ &= 2(-16.66 \text{ kJ}) - 0 - 3(0) = \mathbf{-33.32 \text{ kJ}}\end{aligned}$$

The definitions, etc. are analogous to our earlier discussion of enthalpy, or H .

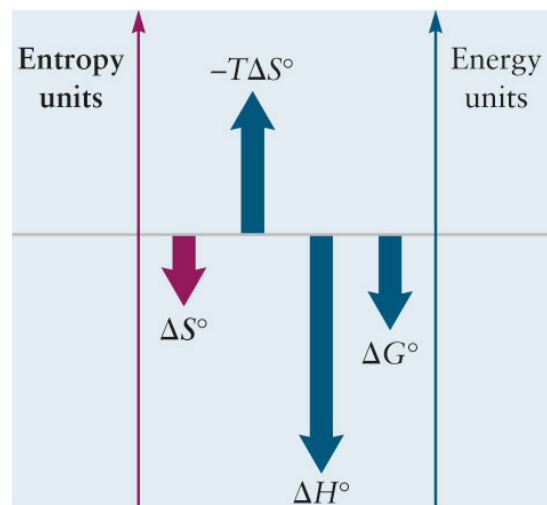
The Gibbs Free Energy, or G

Can think of a few cases about the spontaneous nature of chemical reactions:

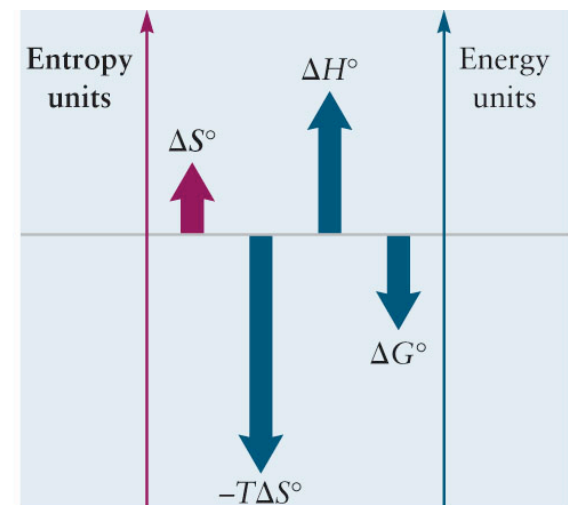
Exothermic reactions (negative ΔH) that increase disorder (positive ΔS) are always spontaneous.

Endothermic reactions (positive ΔH) that decrease disorder (negative ΔS) are never spontaneous.

For cases where the enthalpy and entropy have the same sign, the range of conditions over which the reaction is/can be spontaneous depends on temperature:



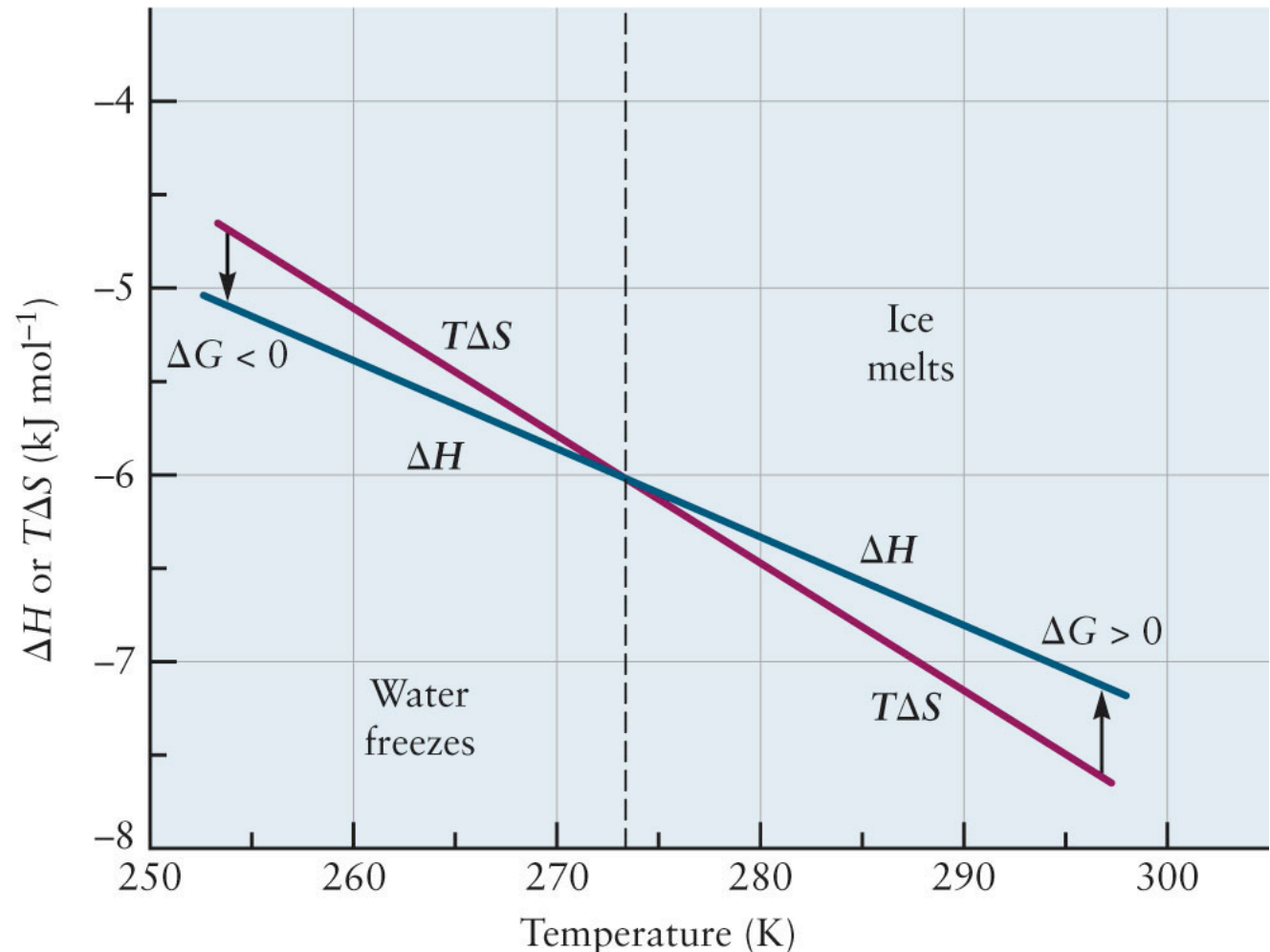
Ammonium nitrate dissolution



The Gibbs Free Energy, or G

Similar concepts can be applied to phase changes, the example in the text is for the freezing of water, where heat is released by the system but where the entropy decreases:

Below 273.15 K the ΔG is negative for freezing and so is spontaneous, while above this temperature it is the reverse process (melting) that is spontaneous.



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:



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

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

The Gibbs Free Energy, or G , and Equilibrium:

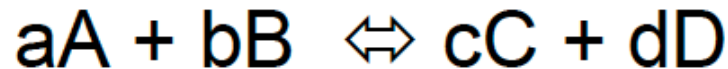
What are the characteristics that have been found that characterize chemical equilibrium:

- They display no macroscopic evidence of change.
- They are reached through spontaneous processes.
- They are the result of a dynamic balance between forward and reverse processes.
- They are the same regardless of the direction of approach to equilibrium.

The Gibbs Free Energy, or G , and Equilibrium:

First some history...

Consider the following general reaction



Regardless of the initial conditions, the value of the ratio

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

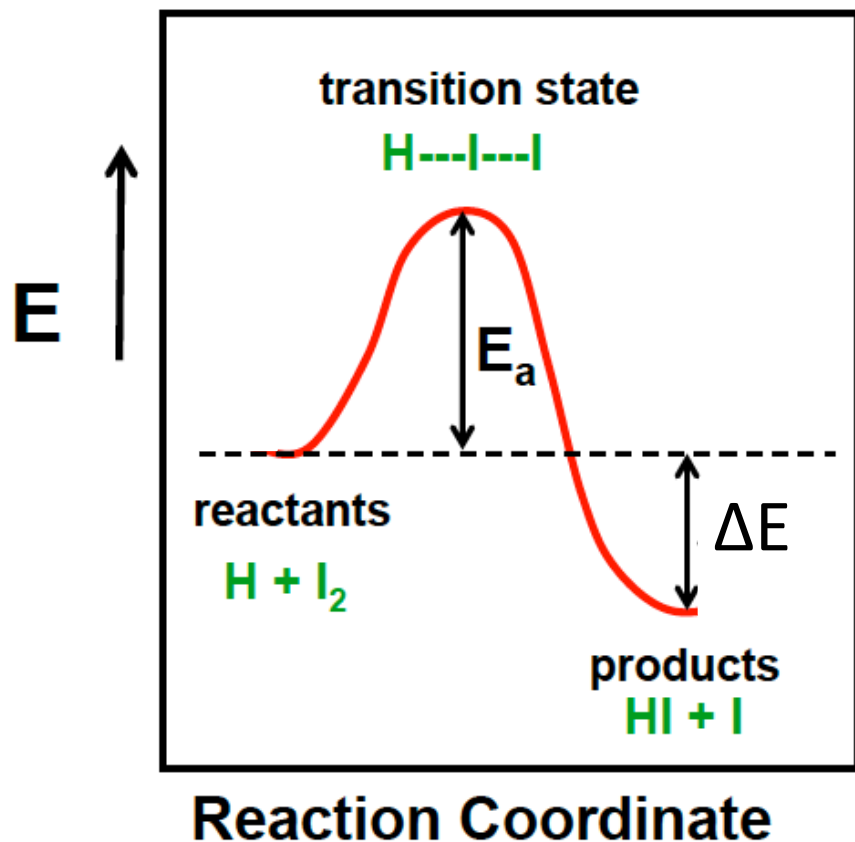
This is called the **law of mass action**, and was discovered through extensive experimentation.

Reaction Coordinates

Before we apply the concepts associated with the law of mass action, let's cover some of the basic issues related to how chemical reactions proceed.

We start with reaction coordinate diagrams, which we will come back to in our discussion of chemical kinetics.

Reaction Coordinates

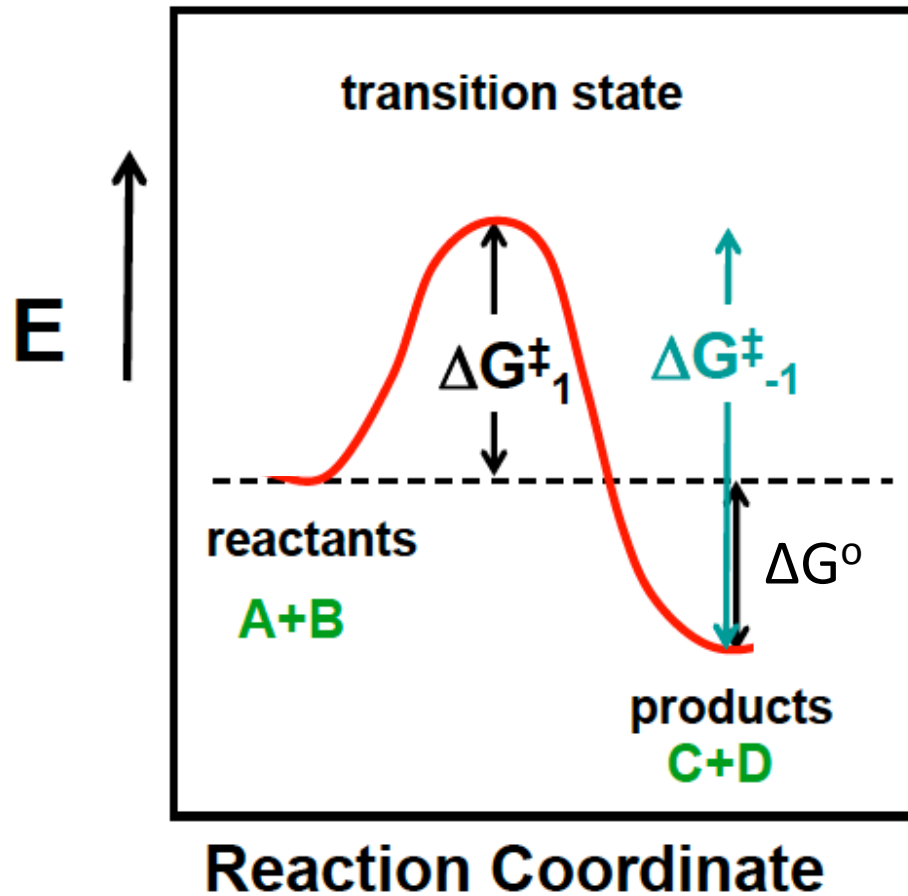


E_a = energy of activation
(not a state function)

ΔE = energy difference
(usually ΔG) between
reactants and products
(a state function)

Reaction Coordinates

Assume $aA + bB \rightleftharpoons cC + dD$ in the gas phase, then



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

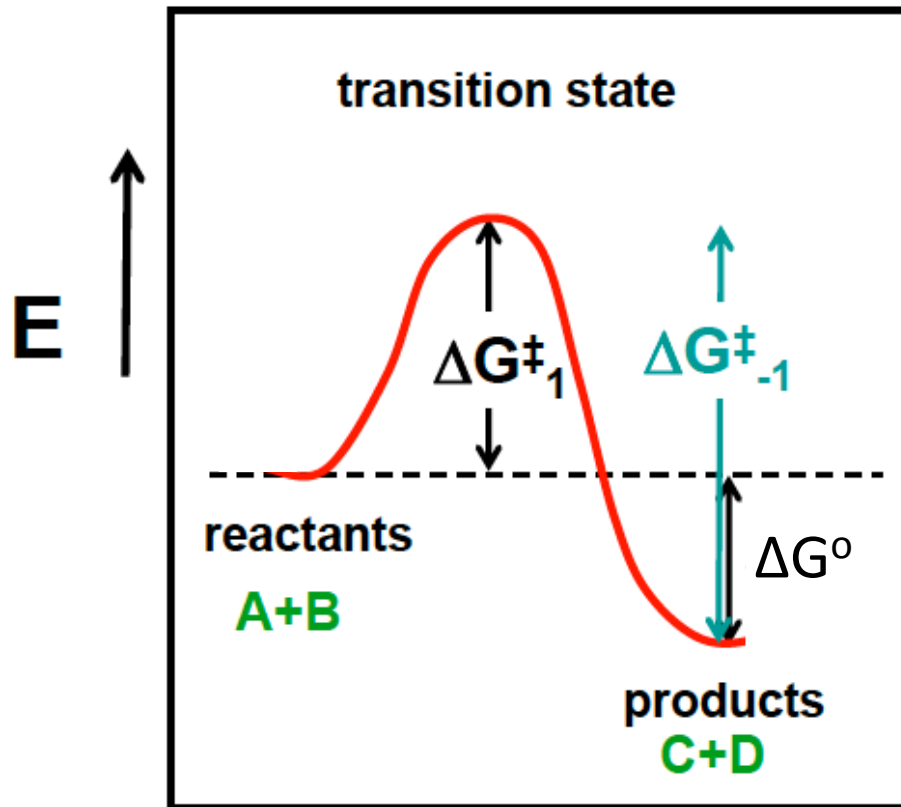
ΔG° = Gibbs free energy difference between reactants & products

ΔG^\ddagger_1 = energy barrier separating reactants & products in the forward direction – **sort of like E_a**

ΔG^\ddagger_{-1} = energy barrier separating reactants & products in the reverse direction

Reaction Coordinates

For the reaction $aA + bB \rightleftharpoons cC + dD$



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

In solution, $K = K_C$

& has units of **[concentration]^{c+d-a-b}**

In the gas phase, $K = K_P$

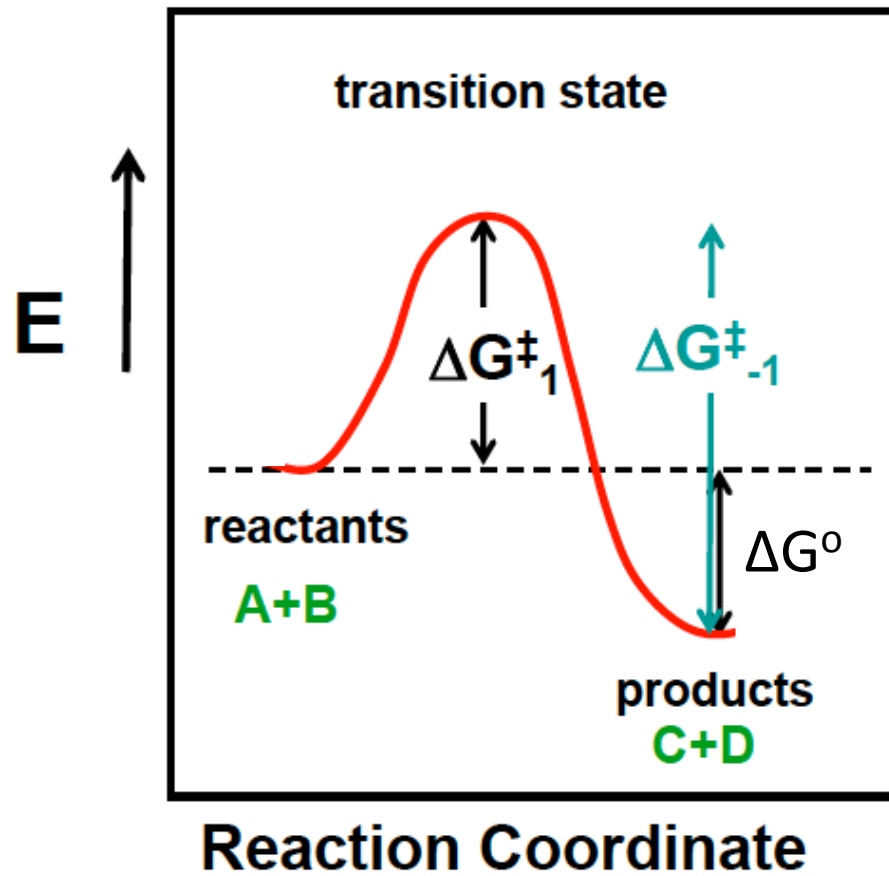
& has units of **[pressure]^{c+d-a-b}**

Reaction Coordinate

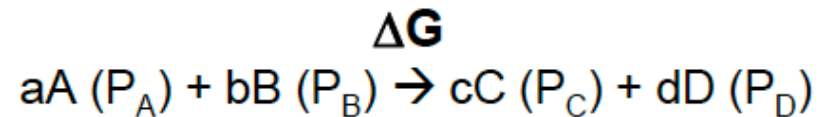
Here we will focus on gas phase equilibria, but the arguments we make are general.

Equilibrium and ΔG°

For the gas phase reaction $aA + bB \rightleftharpoons cC + dD$



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

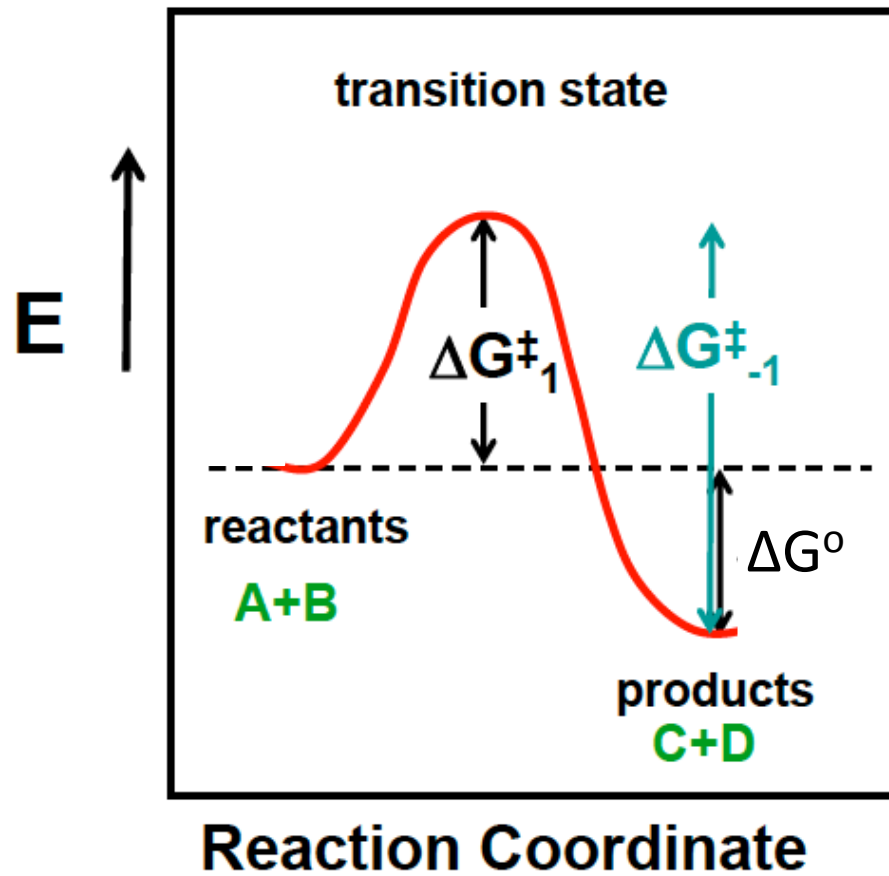


If $\Delta G < 0$, the reaction is spontaneous and it will proceed to the right.
How do we find out if $\Delta G < 0$ or not?

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

Equilibrium and ΔG°

For the gas phase reaction $aA + bB \rightleftharpoons cC + dD$



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

Assume

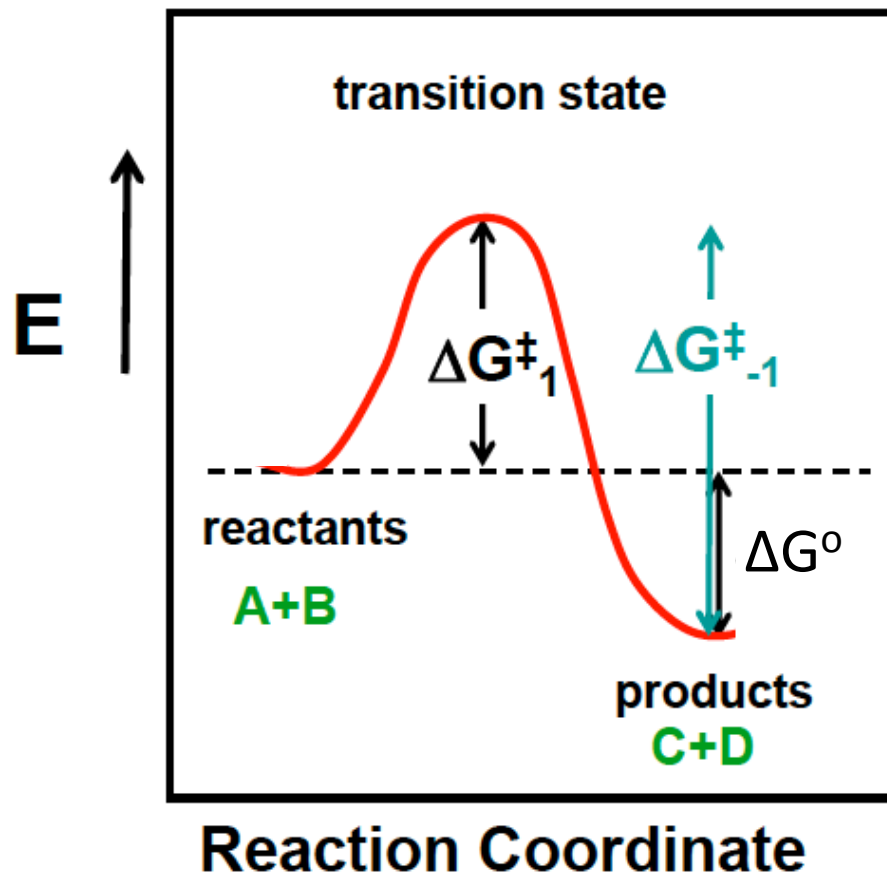
- all products and reactants are ideal gases,
- the initial pressure is P_1 ,
- the final pressure is P_2 ,
- $\Delta T = 0$; $T = 298K$

Then

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

Equilibrium and ΔG^0

For the gas phase reaction $aA + bB \rightleftharpoons cC + dD$



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

Assume

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

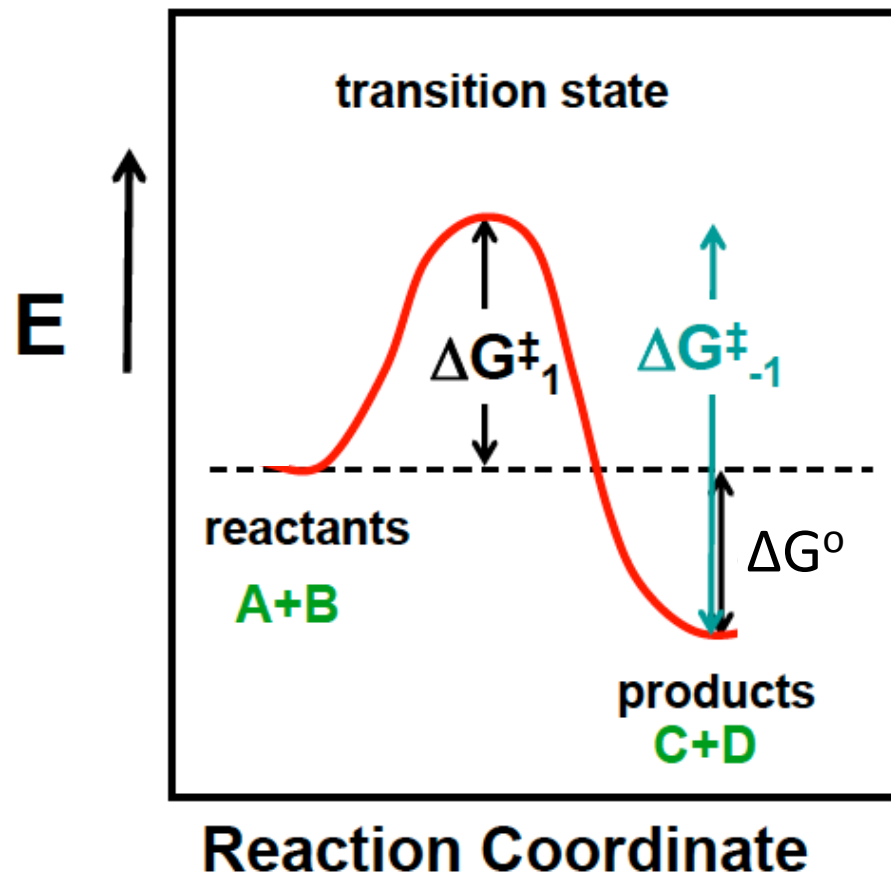
Then

$$\Delta G = \Delta(H - TS) = \cancel{\Delta H} - T\Delta S$$

$$\Delta H = 0 \text{ (isothermal process)}$$

Equilibrium and ΔG°

For the gas phase reaction $aA + bB \rightleftharpoons cC + dD$



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

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

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:

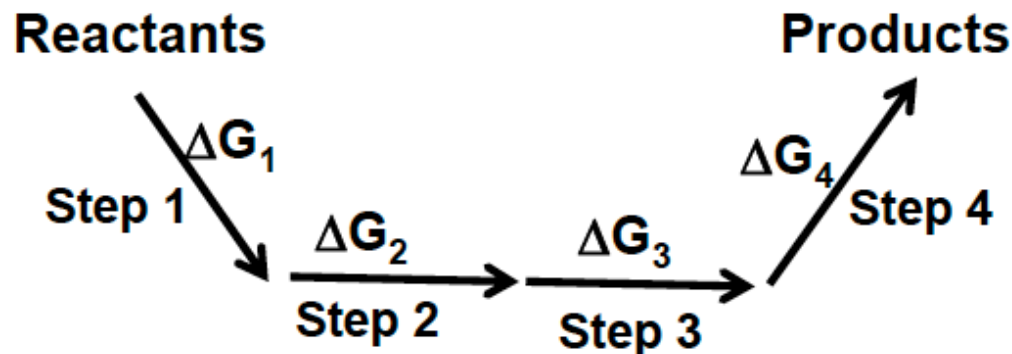
$$\Delta G = -T\Delta S = nRT \ln \left(\frac{P_2}{P_1} \right)$$

Equilibrium and ΔG°

For the gas phase reaction $aA + bB \rightleftharpoons cC + dD$

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

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



$$\Delta G = \sum_{i=1}^4 \Delta G_i$$

If four steps are involved, etc.