

# Chapter 14 (and 15.4): Entropy and Free Energy

Key topics:

**Spontaneous processes**

**Entropy  $S$**

**Gibbs free energy  $G$**

*Begin with a review of some key ideas from Chapter 10*

Why do we “run” chemical reactions?

- we want the products of the reaction
- we want the energy from the reaction

**Thermodynamics**

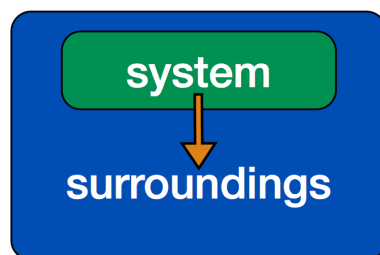
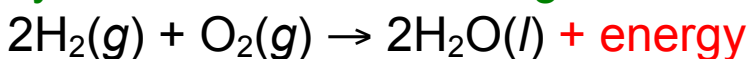
- study of the interconversion of different forms of energy
- separate the universe into system and surroundings

The *system* is the part of the universe that is of interest, including the substances involved in a chemical reaction.

The *surroundings* are everything else.

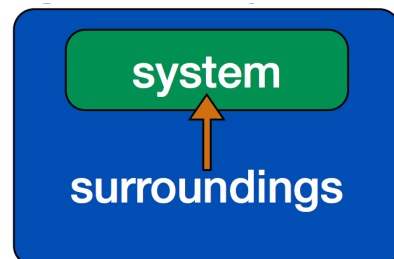
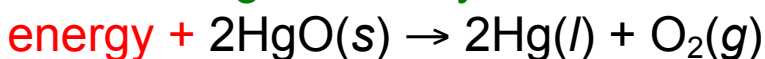
**Exothermic reaction:**

Energy transferred from the system to the surroundings.



**Endothermic reaction:**

Energy transferred from the surroundings to the system.



## First law of thermodynamics: conservation of energy

Energy cannot be created or destroyed:  $\Delta U_{\text{universe}} = 0$

$$\Delta U_{\text{universe}} = \Delta U_{\text{sys}} + \Delta U_{\text{surr}} \Rightarrow \Delta U_{\text{sys}} = -\Delta U_{\text{surr}}$$

Any process that causes energy to be exchanged between the system and the surroundings can be classified as either heat or work.

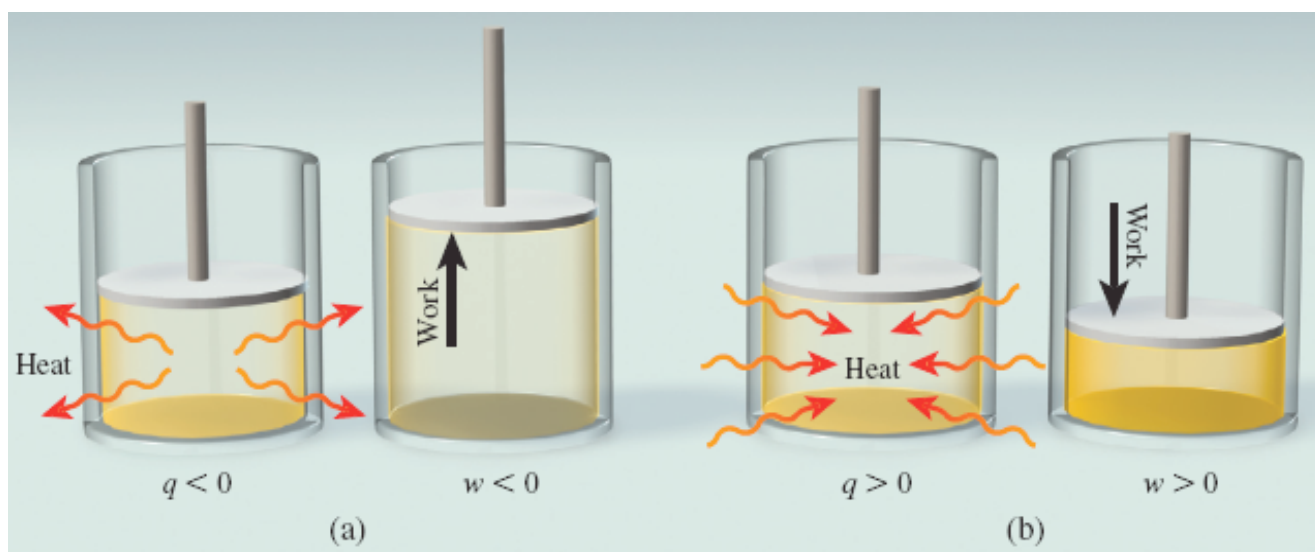
$$\Delta U = q + w$$

$q$  is heat

- $q > 0$ , system absorbs heat
- $q < 0$ , system releases heat

$w$  is work

- $w > 0$ , work is done on the system
- $w < 0$ , work is done by the system



Enthalpy,  $H = U + PV$

- thermodynamic state function
- cannot be measured directly
- at constant pressure,  $\Delta H = q$

Enthalpy of reaction

- $\Delta H = \Delta H_{\text{rxn}} = \Delta H_{\text{products}} - \Delta H_{\text{reactants}}$
- $\Delta H > 0$ , endothermic reaction
- $\Delta H < 0$ , exothermic reaction

Standard enthalpies of formation,  $\Delta H_f^\circ$

- heat change that results when 1 mole of a compound is formed from its constituent elements in their standard states
- standard state is the most stable state found at 1 atm
- $\Delta H_f^\circ$  for elements in their most stable state are zero
- $\Delta H_f^\circ$  for many substances are found in Appendix 2

Standard enthalpy of reaction,  $\Delta H_{\text{rxn}}^\circ$

For the generic chemical reaction



$$\Delta H_{\text{rxn}}^\circ = [c\Delta H_f^\circ(C) + d\Delta H_f^\circ(D)] - [a\Delta H_f^\circ(A) + b\Delta H_f^\circ(B)]$$

## Spontaneous Processes

Spontaneous process:

*does* occur under a specific set of conditions

Non-spontaneous process:

*does not* occur under a specific set of conditions

TABLE 14.1		Familiar Spontaneous and Nonspontaneous Processes	
Spontaneous		Nonspontaneous	
Ice melting at room temperature		Water freezing at room temperature	
Sodium metal reacting violently with water to produce sodium hydroxide and hydrogen gas [Section 8.5]		Sodium hydroxide reacting with hydrogen gas to produce sodium metal and water	
A ball rolling downhill		A ball rolling uphill	
The rusting of iron at room temperature		The conversion of rust back to iron metal at room temperature	
Water freezing at $-10^{\circ}\text{C}$		Ice melting at $-10^{\circ}\text{C}$	

(note: a spontaneous process might occur quickly or slowly)

In Chem 1311, we used enthalpy ( $\Delta H$ ) to predict spontaneity.

- $\Delta H < 0$  (exothermic): spontaneous
- $\Delta H > 0$  (endothermic): not spontaneous

But  $\Delta H$  is not always a good guide.

- water evaporates  
( $\Delta H > 0$  but spontaneous)
- water does not freeze at room temperature  
( $\Delta H < 0$  but not spontaneous)
- ammonium nitrate dissolves in water [cold packs]  
( $\Delta H > 0$  but spontaneous)

Something else must matter...

what else is changing?

- water evaporates:  
*the system's energy is more spread out (in space)*
- water does not freeze at room temperature:  
*the system's energy would become less spread out because the solid (ice) has less freedom of movement than the liquid (water)*
- ammonium nitrate dissolves in water:  
*the system's energy is more spread out because the ionic compound (solid) breaks into soluble ions*

**Entropy (S):** a measure of how spread out or dispersed the system's energy is

More spread out or dispersed = increased entropy ( $\Delta S > 0$ )

Nature tends to move towards states corresponding to an increase in entropy.

Quantitative definition of entropy (Boltzmann)

$$S = k \ln W$$

- $k$  = Boltzmann constant ( $k = R / N_A = 1.38 \times 10^{-23} \text{ J K}^{-1}$ )
- $W$  = number of energetically equivalent microstates

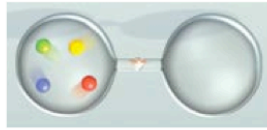
**Macrostate:** thermodynamic state of the system ( $P, T, V, n, U$ )

**Microstates:**

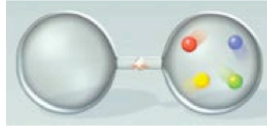
- specific arrangement of particles
- many microstates correspond to *one* macrostate
- we need to "count" the number of microstates  $W$  that correspond to the macrostate (to get the entropy)

Consider the arrangement of 4 gas particles into 2 bulbs.

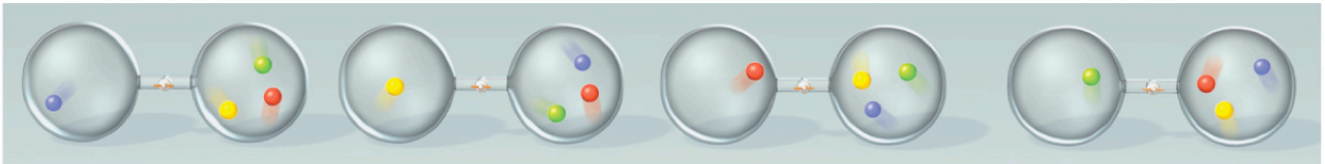
- all 4 in left side:



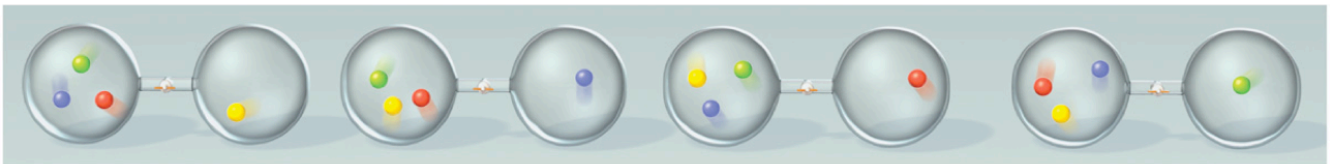
- all 4 in right side:



- one on left side:

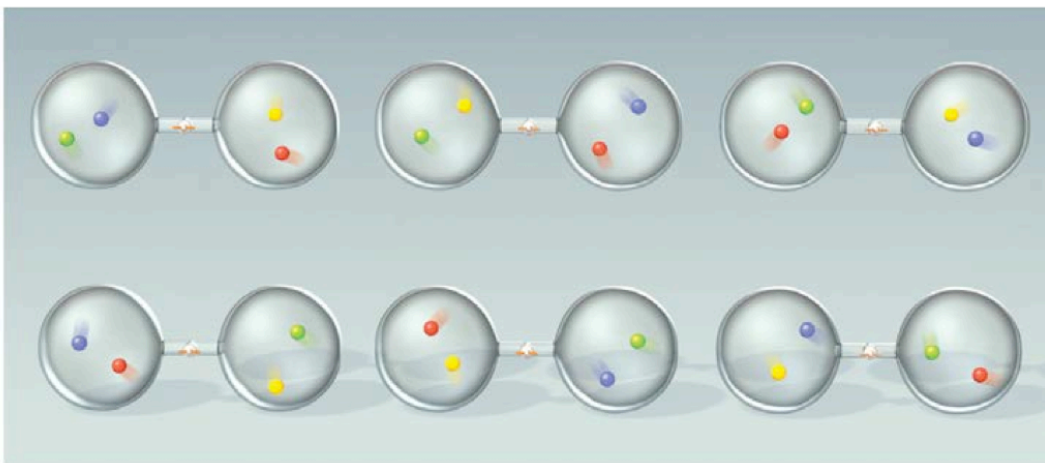


- one on right side:



- two on each side:

**MOST PROBABLE**



The distribution with the largest number of (energetically equivalent) microstates is the most probable. It also has the most dispersed energy state (highest entropy).

Entropy is a state function just like enthalpy

$$\Delta S = S_{\text{final}} - S_{\text{initial}}$$

and processes that increase the number of microstates correspond to more probable states and are favorable ( $\Delta S > 0$ )

- increase in entropy is favorable (spontaneous)

**Standard Entropy ( $S^\circ$ ):** the absolute entropy of a substance at 1 atm (and typically at 25°C)

TABLE 14.2		Standard Entropy Values ( $S^\circ$ ) for Some Substances at 25°C	
Substance	$S^\circ$ (J/K · mol)	Substance	$S^\circ$ (J/K · mol)
H <sub>2</sub> O(l)	69.9	C(diamond)	2.4
H <sub>2</sub> O(g)	188.7	C(graphite)	5.69
Na(s)	51.05	O <sub>2</sub> (g)	205.0
Na(l)	57.56	O <sub>3</sub> (g)	237.6
Na(g)	153.7	F <sub>2</sub> (g)	203.34
He(g)	126.1	Au(s)	47.7
Ne(g)	146.2	Hg(l)	77.4

Note that the units are J K<sup>-1</sup> mol<sup>-1</sup> (vs. kJ mol<sup>-1</sup> for enthalpies)

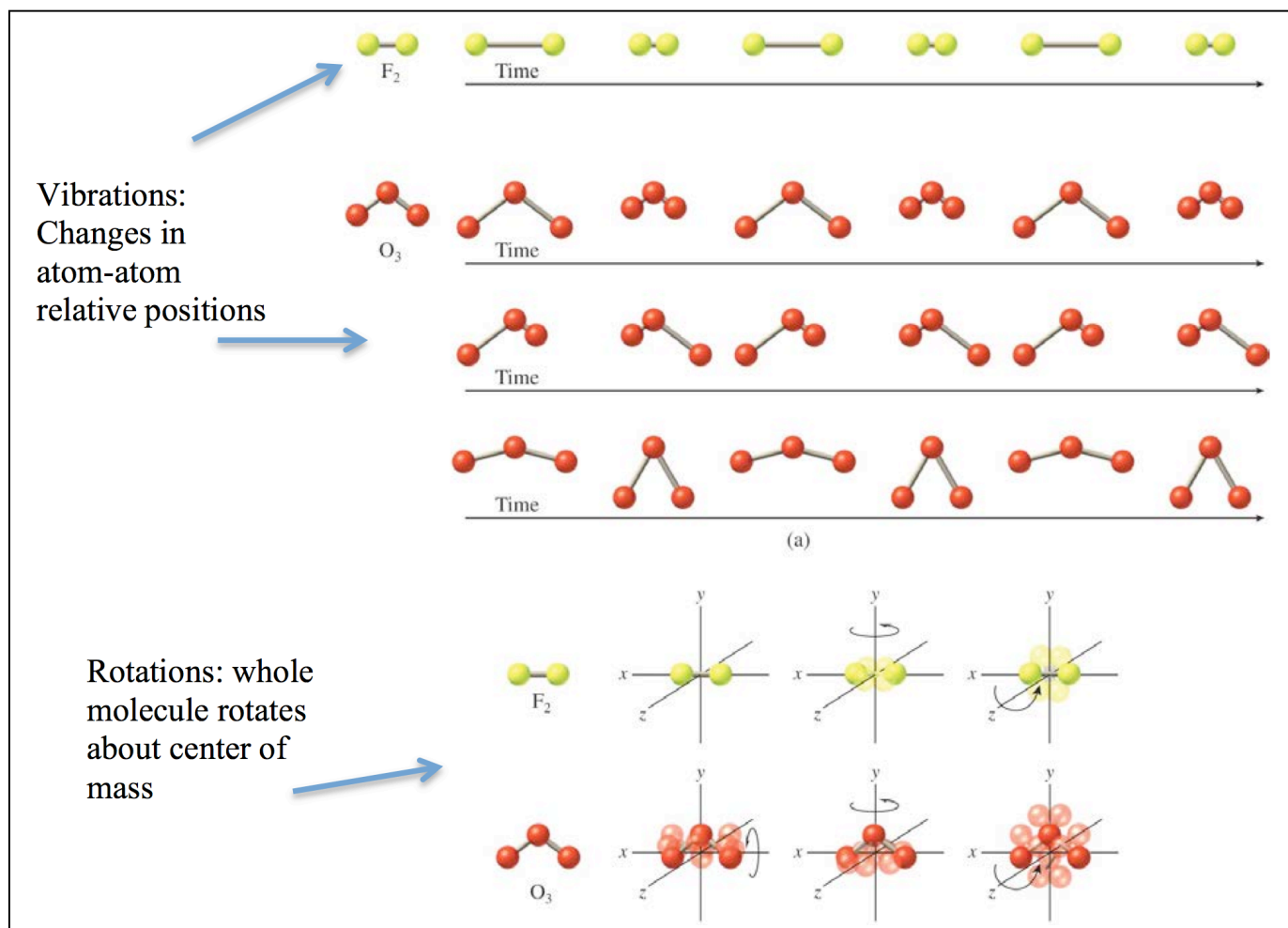
Standard entropies are always positive  
(even for elements in their standard states, unlike  $\Delta H^\circ_f$ )

## Important trends:

1.  $S^\circ$  for the gas phase is greater than the liquid or solid phase of the same substance



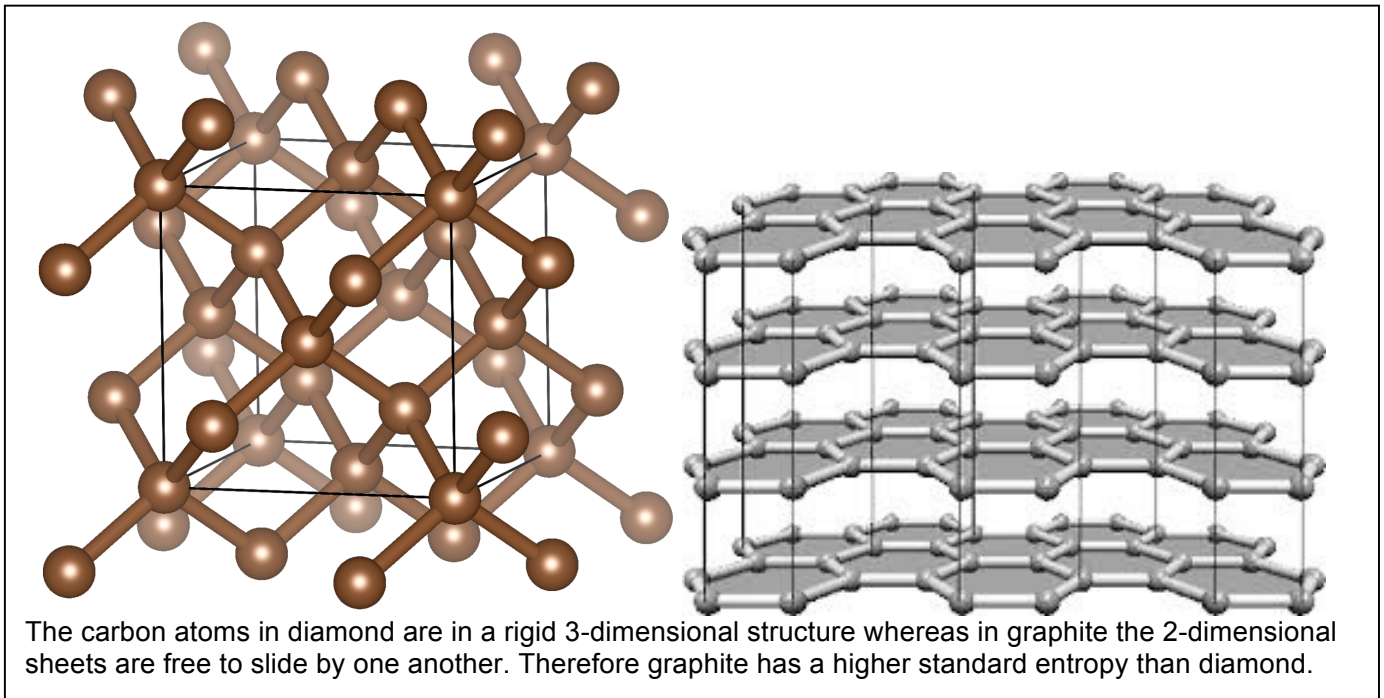
2. More complex structures have greater  $S^\circ$  (with a similar molar mass, same phase) because more types of motion are possible





### 3. Allotropes: the more ordered forms have lower $S^\circ$

Diamond has lower  $S^\circ$  than graphite



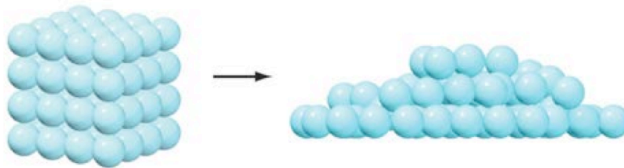
### 4. Monatomic species: the heavier atom has greater $S^\circ$

helium has lower  $S^\circ$  than neon

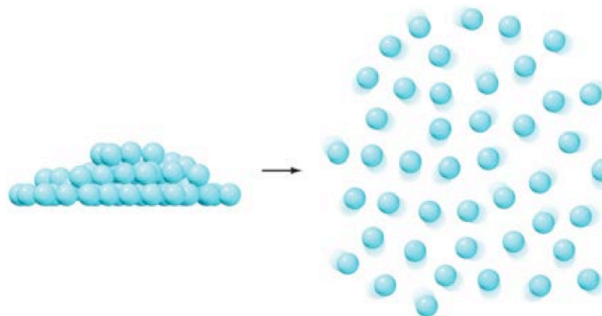
(due to quantization of translational energy; higher mass corresponds to more closely spaced energy levels)

## Entropy changes in a system

○  $S^\circ_{\text{liquid}} > S^\circ_{\text{solid}}$



○  $S^\circ_{\text{vapor}} > S^\circ_{\text{liquid}}$



○  $S^\circ_{\text{aqueous}} > S^\circ_{\text{pure solid}}$

Hydrated ions organize the water around them which leads to a decrease in solvent entropy.

When the charges are small ( $\pm 1$ ) the solute entropy dominates ( $S^\circ_{\text{system}} > 0$ ), but

when the charges are large (e.g.,  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ) the solvent (water) entropy can dominate, leading to  $S^\circ_{\text{system}} < 0$

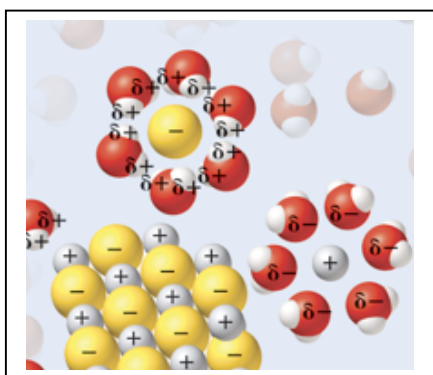
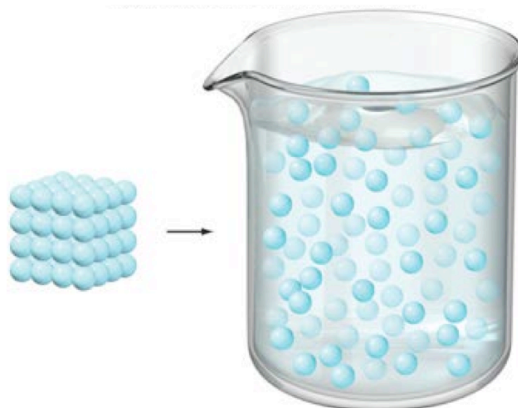
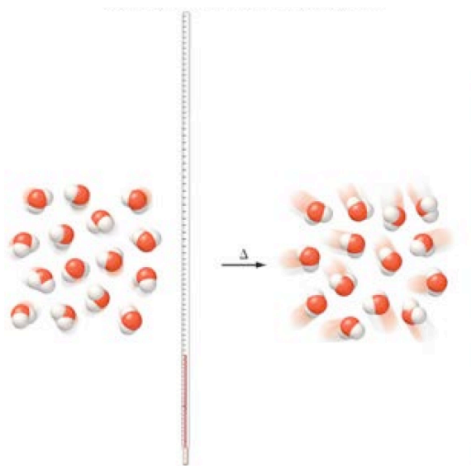


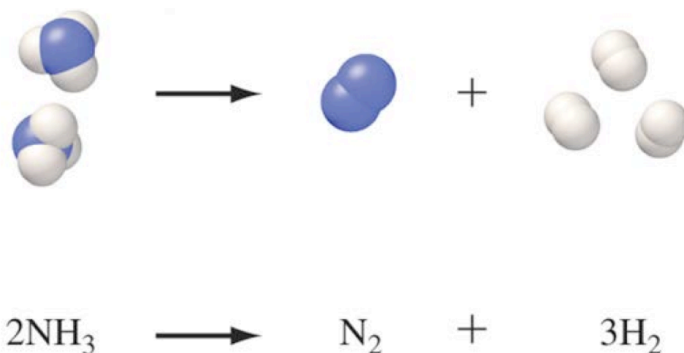
TABLE 14.3		Entropy Changes for the Dissolution ( $\Delta S^\circ_{\text{soln}}$ ) of Some Ionic Solids at 25°C
Dissolution equation		$\Delta S^\circ_{\text{soln}}$ (J/K · mol)
$\text{NH}_4\text{NO}_3(s) \longrightarrow \text{NH}_4^+(aq) + \text{NO}_3^-(aq)$		108.1
$\text{AlCl}_3(s) \longrightarrow \text{Al}^{3+}(aq) + 3\text{Cl}^-(aq)$		-253.2
$\text{FeCl}_3(s) \longrightarrow \text{Fe}^{3+}(aq) + 3\text{Cl}^-(aq)$		-266.1

e.g., Make a qualitative prediction of the sign of  $\Delta H^\circ_{\text{soln}}$  for  $\text{AlCl}_3(s)$

○  $S^\circ_{\text{higher temp}} > S^\circ_{\text{lower temp}}$



○  $S^\circ_{\text{more moles gas}} > S^\circ_{\text{fewer moles gas}}$



○  $S^\circ_{\text{larger volume of gas}} > S^\circ_{\text{smaller volume of gas}}$

e.g., Determine the sign of  $\Delta S$  for the following (qualitatively)

1. Liquid nitrogen evaporates.
2. Aqueous solutions of potassium iodide and lead nitrate are mixed together.
3. Water is heated from room temperature to  $60^\circ\text{C}$ .

# Entropy Changes in the Universe and The Second and Third Laws of Thermodynamics

The universe is composed of two parts:

- the system
- the surroundings (everything else)

Both parts undergo changes in  $S$  during physical and chemical processes

*Second Law of Thermodynamics:* the entropy of the universe increases in a spontaneous process and remains unchanged in an equilibrium process.

Spontaneous:  $\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$

$\Delta S_{\text{system}}$  can be negative as long as  $\Delta S_{\text{surroundings}}$  is more positive

Equilibrium process:  $\Delta S_{\text{universe}} = 0$

e.g., water freezing at  $0^\circ\text{C}$ ; chemical reaction where  $Q = K$ .

*Entropy changes in the system:*

Entropy can be calculated from a table of standard values just as enthalpy changes were calculated.

For the general reaction



$$\Delta S_{\text{rxn}}^\circ = [cS^\circ(\text{C}) + dS^\circ(\text{D})] - [aS^\circ(\text{A}) + bS^\circ(\text{B})]$$

## Entropy changes in the surroundings:

We know how to calculate  $\Delta S_{\text{system}}^{\circ} = \Delta S_{\text{rxn}}^{\circ}$

What about  $\Delta S_{\text{surroundings}}$  ?

Consider liquid water freezing below  $0^{\circ}\text{C}$

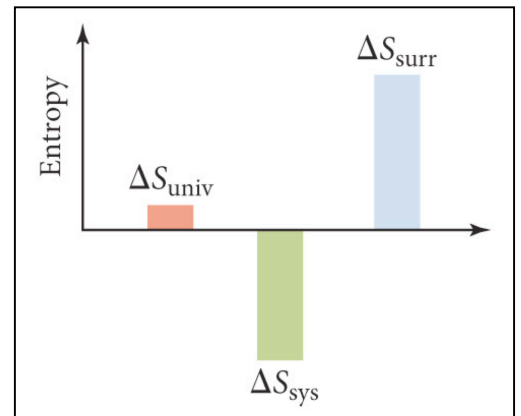
spontaneous,  $\Delta S_{\text{universe}} > 0$

liquid  $\rightarrow$  solid,  $\Delta S_{\text{system}} < 0$

Therefore  $|\Delta S_{\text{surr}}| > |\Delta S_{\text{sys}}|$

How does water freezing increase  $S_{\text{surr}}$  ?

- water freezing is exothermic
- energy is being dispersed into the surroundings



$\Delta S_{\text{surr}} > 0$  for exothermic processes

$\Delta S_{\text{surr}} < 0$  for endothermic processes

Therefore

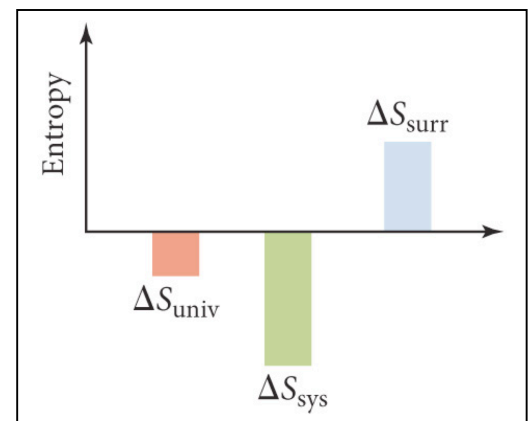
$$\Delta S_{\text{surroundings}}^{\circ} \propto -\Delta H_{\text{system}} \quad (\propto -q)$$

But water freezing above  $0^{\circ}\text{C}$  is not spontaneous.

The magnitude of  $\Delta S_{\text{surr}}$  depends on the temperature

- $T < 0^{\circ}\text{C}$ ,  $|\Delta S_{\text{surr}}| > |\Delta S_{\text{sys}}|$
- $T > 0^{\circ}\text{C}$ ,  $|\Delta S_{\text{surr}}| < |\Delta S_{\text{sys}}|$
- but  $\Delta S_{\text{sys}}$  is virtually independent of  $T$
- thus  $|\Delta S_{\text{surr}}|$  depends on  $T$
- $\Delta S_{\text{surr}}$  is inversely proportional to  $T$

$$\Delta S_{\text{surr}}^{\circ} \propto \frac{1}{T}$$

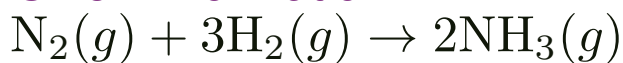


Combining these two relations gives

$$\Delta S_{\text{surr}}^{\circ} = -\frac{\Delta H_{\text{sys}}}{T}$$

e.g., Predict if the synthesis of ammonia at 25°C is spontaneous or not.

Given information:



$$\Delta H_{\text{rxn}}^{\circ} = -92.6 \text{ kJ/mol}$$

$$S^{\circ}[\text{N}_2(g)] = 191.5 \text{ J K}^{-1}\text{mol}^{-1}$$

$$S^{\circ}[\text{H}_2(g)] = 131.0 \text{ J K}^{-1}\text{mol}^{-1}$$

$$S^{\circ}[\text{NH}_3(g)] = 193.0 \text{ J K}^{-1}\text{mol}^{-1}$$

Solution:

$$\Delta S_{\text{sys}} = \Delta S_{\text{rxn}} = 2(193.0) - (191.5) - 3(131.0) = -198.5 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta S_{\text{surr}} = -(-92.6 \text{ kJ mol}^{-1}) / 298 \text{ K} = 311 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta S_{\text{universe}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 112 \text{ J K}^{-1} \text{ mol}^{-1} \quad \text{spontaneous}$$

e.g., Calculate  $\Delta S_{\text{universe}}$  and determine the spontaneity of the reaction  $\text{H}_2\text{O}_2(l) \rightarrow \text{H}_2\text{O}_2(g)$  at 163°C.

Given information (from Appendix 2):

$$S^{\circ}[\text{H}_2\text{O}_2(l)] = 109.6 \text{ J K}^{-1}\text{mol}^{-1}$$

$$\Delta H_{\text{f}}^{\circ}[\text{H}_2\text{O}_2(l)] = -187.6 \text{ kJ mol}^{-1}$$

$$S^{\circ}[\text{H}_2\text{O}_2(g)] = 232.9 \text{ J K}^{-1}\text{mol}^{-1}$$

$$\Delta H_{\text{f}}^{\circ}[\text{H}_2\text{O}_2(g)] = -136.1 \text{ kJ mol}^{-1}$$

Solution:

$$\Delta H_{\text{rxn}} = -136.1 - (-187.6) = 51.5 \text{ kJ mol}^{-1}$$

$$\Delta S_{\text{surr}} = -(51.5 \text{ kJ mol}^{-1}) / 436 \text{ K} = -118 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta S_{\text{sys}} = \Delta S_{\text{rxn}} = 232.9 - 109.6 = 123.3 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta S_{\text{universe}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 5.3 \text{ J K}^{-1} \text{ mol}^{-1} \quad \text{spontaneous}$$

e.g., The reaction  $\text{NH}_3(g) + \text{HCl}(g) \rightarrow \text{NH}_4\text{Cl}(s)$  is spontaneous at room temperature. Determine the temperature at which it is no longer spontaneous.

Given information (from Appendix 2):

$$\begin{array}{ll} S^\circ[\text{NH}_3(g)] = 193.0 \text{ J K}^{-1}\text{mol}^{-1} & \Delta H_f^\circ[\text{NH}_3(g)] = -46.3 \text{ kJ mol}^{-1} \\ S^\circ[\text{HCl}(g)] = 187.0 \text{ J K}^{-1}\text{mol}^{-1} & \Delta H_f^\circ[\text{HCl}(g)] = -92.3 \text{ kJ mol}^{-1} \\ S^\circ[\text{NH}_4\text{Cl}(s)] = 94.56 \text{ J K}^{-1}\text{mol}^{-1} & \Delta H_f^\circ[\text{NH}_4\text{Cl}(s)] = -315.39 \text{ kJ mol}^{-1} \end{array}$$

Solution:

$$\Delta H_{\text{rxn}} = -315.4 - (-46.3 - 92.3) = -176.8 \text{ kJ mol}^{-1}$$

$$\Delta S_{\text{sys}} = \Delta S_{\text{rxn}} = 94.56 - (193.0 + 187.0) = -285.44 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta S_{\text{universe}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = -0.28544 + (176.8 / T) > 0$$

This inequality holds as long as  $T < 176.8 / 0.28544 = 619 \text{ K}$

e.g., Determine the boiling point of  $\text{Br}_2$ .

Given information (from Appendix 2):

$$\begin{array}{ll} S^\circ[\text{Br}_2(l)] = 152.3 \text{ J K}^{-1}\text{mol}^{-1} & \Delta H_f^\circ[\text{Br}_2(l)] = 0 \text{ kJ mol}^{-1} \\ S^\circ[\text{Br}_2(g)] = 245.13 \text{ J K}^{-1}\text{mol}^{-1} & \Delta H_f^\circ[\text{Br}_2(g)] = 30.7 \text{ kJ mol}^{-1} \end{array}$$

Solution:

For the equilibrium  $\text{Br}_2(l) \rightleftharpoons \text{Br}_2(g)$

$$\Delta H_{\text{rxn}} = 30.7 \text{ kJ mol}^{-1}$$

$$\Delta S_{\text{sys}} = \Delta S_{\text{rxn}} = 245.13 - 152.3 = 92.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

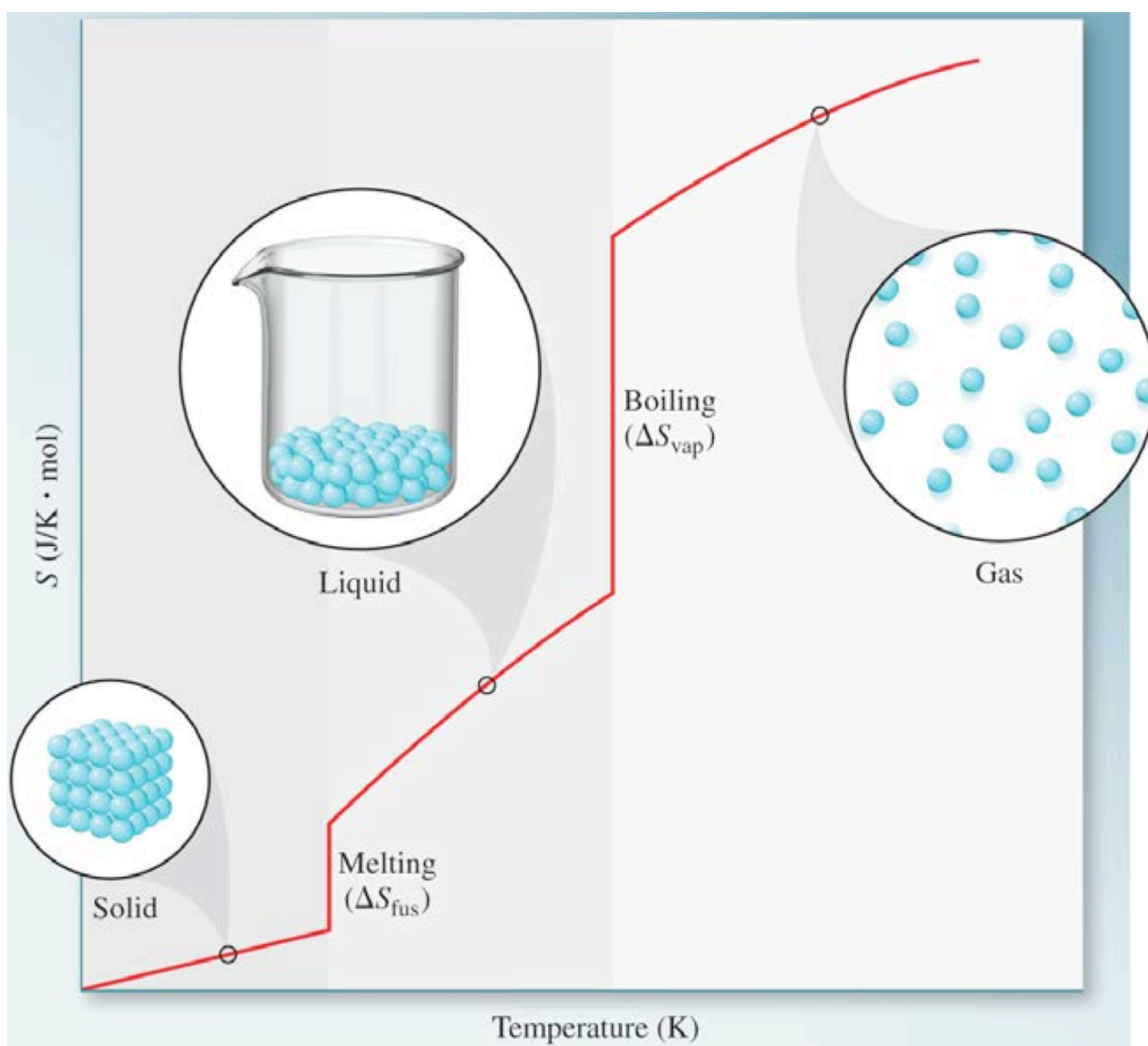
$$\Delta S_{\text{universe}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0 \Rightarrow T = 331 \text{ K} = 58^\circ\text{C}$$

## Third law of thermodynamics

The entropy of a perfect crystalline substance at  $T = 0 \text{ K}$  is zero.

$$S = k \ln W = k \ln 1 = 0$$

The importance of this law is that it allows us to calculate absolute entropy values ( $S^\circ$ )





## Gibbs Free Energy

Recall that the 2<sup>nd</sup> Law of Thermodynamics says that a process is spontaneous if  $\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$

It would be convenient if we could predict spontaneity based *only* on what happens to the system.

We can do this using  $\Delta S_{\text{surr}} = -\Delta H_{\text{sys}} / T$  because then

$\Delta S_{\text{universe}} = \Delta S_{\text{sys}} - \Delta H_{\text{sys}} / T > 0$ , or

$T\Delta S_{\text{sys}} - \Delta H_{\text{sys}} > 0$ , or

$\Delta H_{\text{sys}} - T\Delta S_{\text{sys}} < 0$

Based on this inequality, we define the Gibbs Free Energy as

$$G = H - TS$$

At constant temperature and pressure ( $\Delta H = q$ ), we have (where all terms are for the system):

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

$\Delta G < 0 \Rightarrow$  spontaneous in the forwards direction

$\Delta G > 0 \Rightarrow$  NOT spontaneous in the forwards direction

$\Delta G = 0 \Rightarrow$  the system is at equilibrium

Case 1:  $\Delta H < 0$  and  $\Delta S > 0$

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

$$= (-) - T(+)$$

$$< 0 \text{ always}$$

e.g.,  $2\text{H}_2\text{O}_2(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$

Case 2:  $\Delta H > 0$  and  $\Delta S < 0$

$$\begin{aligned}\Delta G &= \Delta H - T\Delta S \\ &= (+) - T(-) \\ &> 0 \text{ always}\end{aligned}$$

e.g.,  $3\text{O}_2(g) \rightarrow 2\text{O}_3(g)$

Case 3:  $\Delta H > 0$  and  $\Delta S > 0$

$$\begin{aligned}\Delta G &= \Delta H - T\Delta S \\ &= (+) - T(+)  
< 0 \text{ at high } T\end{aligned}$$

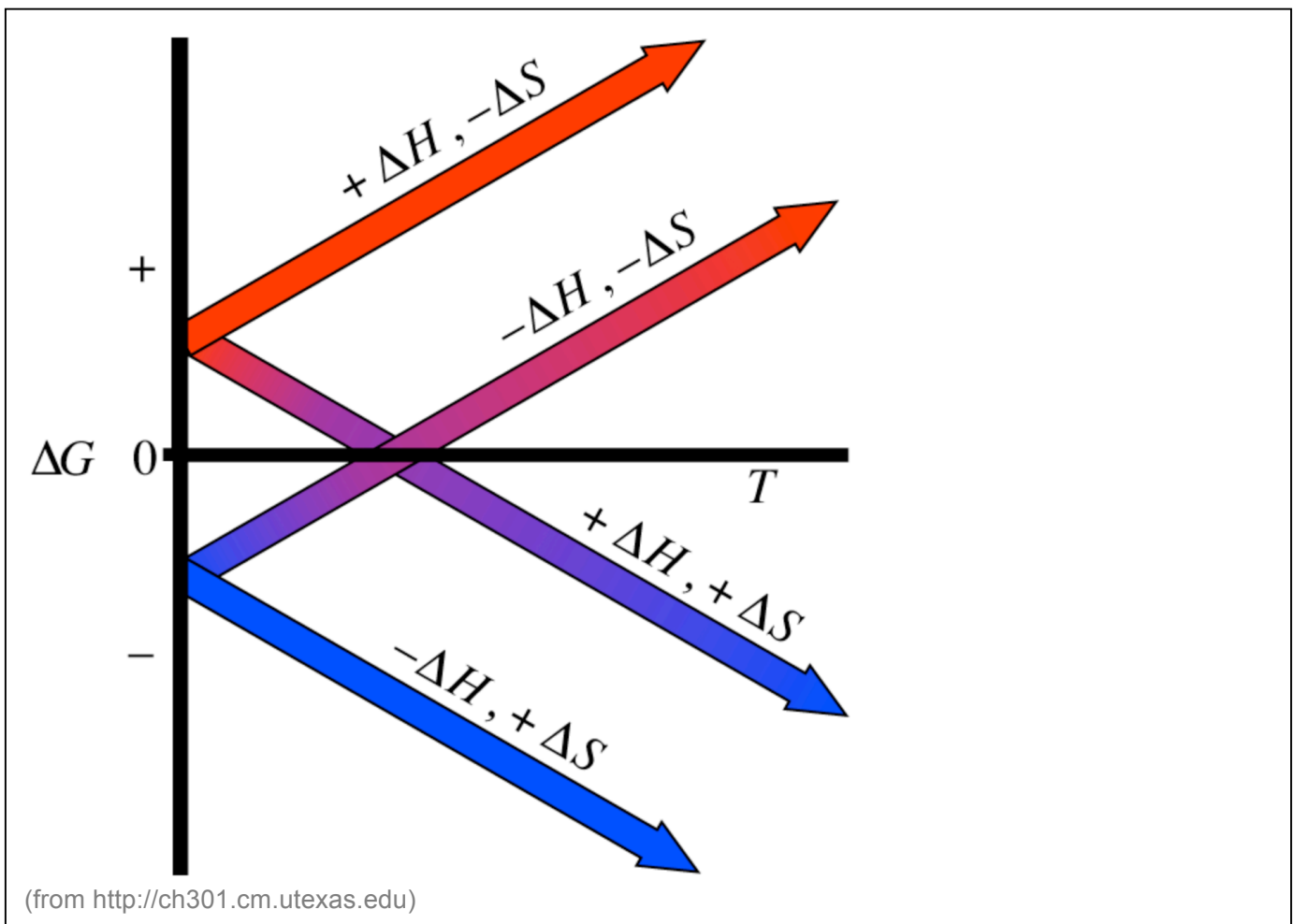
e.g., ice melting; water evaporating

Case 4:  $\Delta H < 0$  and  $\Delta S < 0$

$$\begin{aligned}\Delta G &= \Delta H - T\Delta S \\ &= (-) - T(-)  
< 0 \text{ at low } T\end{aligned}$$

e.g., water freezing; water vapor condensing

<b><math>\Delta G</math> TABLE</b>		<b><math>\Delta S</math> +</b>	<b>-</b>
<b><math>\Delta H</math></b>	<b>+</b>	$\Delta G < 0$ at high T	$\Delta G > 0$ always Spontaneous never (at no T)
	<b>-</b>	$\Delta G < 0$ always Spontaneous always (at all T)	$\Delta G < 0$ at low T



*Determining T required for spontaneity:*

What does “high T” or “low T” mean?

For water, we know the answer:

- water freezing:  $\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(s)$   
spontaneous at low  $T$  (below  $0^\circ\text{C}$ )
- water evaporating:  $\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g)$   
spontaneous at high  $T$  (above  $100^\circ\text{C}$ )

In general, we set  $\Delta G = 0$  (equilibrium condition):

$$0 = \Delta H - T\Delta S \quad \Rightarrow \quad T = (\Delta H) / (\Delta S) \quad T \text{ in Kelvin}$$

Note: for phase changes this relation also allows us to compute the entropy change  $\Delta S = (\Delta H) / (T)$



e.g., The reaction  $4\text{Fe}(s) + 3\text{O}_2(g) + 6\text{H}_2\text{O}(l) \rightleftharpoons 4\text{Fe}(\text{OH})_3(s)$  is spontaneous below  $1950^\circ\text{C}$ . Estimate  $\Delta S^\circ$  for  $\text{Fe}(\text{OH})_3(s)$ .

Given information (from Appendix 2):

$$\begin{aligned} S^\circ[\text{Fe}(s)] &= 27.2 \text{ J K}^{-1}\text{mol}^{-1} & \Delta H_f^\circ[\text{Fe}(s)] &= 0 \text{ kJ mol}^{-1} \\ S^\circ[\text{O}_2(g)] &= 205.0 \text{ J K}^{-1}\text{mol}^{-1} & \Delta H_f^\circ[\text{O}_2(g)] &= 0 \text{ kJ mol}^{-1} \\ S^\circ[\text{H}_2\text{O}(l)] &= 69.9 \text{ J K}^{-1}\text{mol}^{-1} & \Delta H_f^\circ[\text{H}_2\text{O}(l)] &= -285.8 \text{ kJ mol}^{-1} \\ S^\circ[\text{Fe}(\text{OH})_3(s)] &= x \text{ J K}^{-1}\text{mol}^{-1} & \Delta H_f^\circ[\text{Fe}(\text{OH})_3(s)] &= -824.25 \text{ kJ mol}^{-1} \end{aligned}$$

Solution:

From  $\Delta G = \Delta H - T\Delta S$ , at  $T = 1950^\circ\text{C}$  we have  $\Delta S = (\Delta H) / (T)$ .

We must convert to Kelvin and solve for the missing data.

$$\Delta S = 4x - 4(27.2) - 3(205.0) - 6(69.9) = 4x - 1143.2$$

$$\Delta H = 4(-824.25) - 6(-285.8) = -1582.2$$

$$\frac{4x - 1143.2}{1000} = \frac{-1582.2}{1950 + 273} \quad \Rightarrow \quad x = 107.9 \text{ J K}^{-1}\text{mol}^{-1}$$

## Standard free energy changes, $\Delta G^\circ$

The standard free energy change of reaction  $\Delta G^\circ_{\text{rxn}}$  is the  $\Delta G$  value under standard state conditions, which are

- Gases 1 atm pressure
- Liquids pure liquid
- Solids pure solid
- Elements most stable allotrope at 1 atm, 25°C
- Solutions 1 molar concentration

$\Delta G^\circ$  can be calculated from a table of standard values ( $\Delta G^\circ_f$ ) just like enthalpy and entropy values



$$\Delta G^\circ_{\text{rxn}} = [c\Delta G^\circ_f(C) + d\Delta G^\circ_f(D)] - [a\Delta G^\circ_f(A) + b\Delta G^\circ_f(B)]$$

Here  $\Delta G^\circ_f$  is the standard free energy of formation of a compound, namely the free energy change that occurs when 1 mole of the compound is synthesized from its constituent elements, each in their standard state.

Therefore,  $\Delta G^\circ_f = 0$  for elements in their standard states.

$\Delta G^\circ$  values at different temperatures:

In the equation  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

the  $\Delta H^\circ$  and  $\Delta S^\circ$  terms are somewhat insensitive to changes in temperature, so to get a rough estimate of  $\Delta G^\circ$  we can do:

$$\Delta G^\circ_T = \Delta H^\circ_{298} - T\Delta S^\circ_{298}$$

## Chemical Equilibrium and Free Energy

### Relationship between $\Delta G$ and $\Delta G^\circ$

We can get  $\Delta G^\circ$  from tables (Appendix 2) but we need  $\Delta G$  to predict spontaneity. For  $\Delta G$ , there is a relationship with  $Q$  vs  $K$

if  $Q < K$  (or  $Q/K < 1$ )  
or  
 $\Delta G < 0$



reaction  
proceeds to  
right

if  $Q > K$  (or  $Q/K > 1$ )  
or  
 $\Delta G > 0$

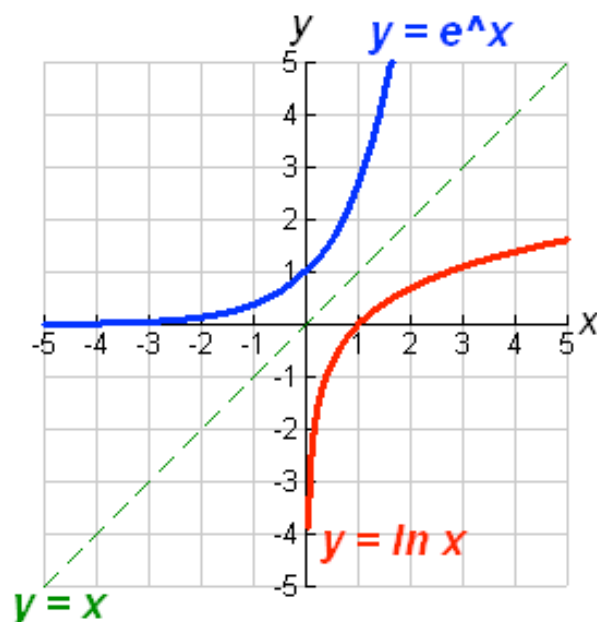


reaction  
proceeds to  
left

if  $Q = K$  (or  $Q/K = 1$ )  
or  
 $\Delta G = 0$



reaction is  
at equilibrium



Notice that  $\ln(Q/K)$  has  
the same sign as  $\Delta G$

In fact, they are proportional to each other

$$\Delta G \propto \ln(Q/K)$$

$$\Delta G = RT \ln(Q/K)$$

$$\Delta G = RT \ln(Q) - RT \ln(K)$$

Now, if we put everything at standard conditions, then

- $\Delta G = \Delta G^\circ$

- $Q = 1$  since all concentrations 1 M, all pressures 1 atm

Therefore we have the relation

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

$K$  is the equilibrium constant, which we can now calculate if we have the available thermodynamic data.

$K$	$\ln K$	$\Delta G^\circ$	Result at equilibrium
$> 1$	Positive	Negative	Products are favored.
$= 1$	0	0	Neither products nor reactants are favored.
$< 1$	Negative	Positive	Reactants are favored.

e.g., Calculate  $\Delta G^\circ$  for  $\text{BaF}_2(\text{s}) \rightleftharpoons \text{Ba}^{2+}(\text{aq}) + 2\text{F}^{-}(\text{aq})$   
given  $K_{\text{sp}} = 1.7 \times 10^{-6}$  for  $\text{BaF}_2(\text{s})$  at  $25^\circ\text{C}$ .

Solution:

$$\begin{aligned}\Delta G^\circ &= -RT \ln K = -(8.314 \times 10^{-3} \text{ kJ mol}^{-1}\text{K}^{-1})(298 \text{ K})(-13.285) \\ &= 32.9 \text{ kJ/mol}\end{aligned}$$

## $\Delta G^\circ$

- is constant for a specific reaction at a specific  $T$
- contains the same information as the magnitude of  $K$
- if we change  $T$ ,  $K$  and  $\Delta G^\circ$  change:  $\Delta G^\circ_T = -RT \ln K_T$

Note: this gives us a new way to predict how temperature affects equilibrium (previously, we used Le Chatelier's Principle based on the sign of  $\Delta H$ )

## $\Delta G$

- contains the same information as  $Q$  vs  $K$  comparison
- equal to the maximum work that can be done (expansion work, electrical work, or chemical work)
- changes as the reaction proceeds ( $\rightarrow$  zero at equilibrium)

Since  $\Delta G^\circ$  is related to the logarithm of  $K$ , small changes in  $\Delta G^\circ$  lead to large changes in  $K$ . We can use this to determine very large or very small  $K$  values from thermodynamic data.

$\Delta G^\circ$ (kJ)	$K$	significance
200	$9 \times 10^{-36}$	Essentially no forward rxn; reverse rxn goes to completion
100	$3 \times 10^{-18}$	
50	$2 \times 10^{-9}$	
10	$2 \times 10^{-2}$	
1	$7 \times 10^{-1}$	
0	1	Forward and reverse rxns proceed to same extent
-1	1.5	
-10	$5 \times 10^1$	
-50	$6 \times 10^8$	
-100	$3 \times 10^{17}$	Forward rxn goes to completion
-200	$1 \times 10^{35}$	essentially no reverse rxn



Put everything together:

$$\Delta G = \underbrace{\Delta G^\circ}_{\text{fixed}} + \underbrace{RT \ln Q}_{\text{varies}} \quad \begin{cases} \Delta G = RT \ln(Q) - RT \ln(K) \\ \Delta G^\circ = -RT \ln K \end{cases}$$



Calculate  $\Delta G$  with initial values  $P_{\text{H}_2} = 5.25 \text{ atm}$ ;  $P_{\text{HI}} = 1.75 \text{ atm}$

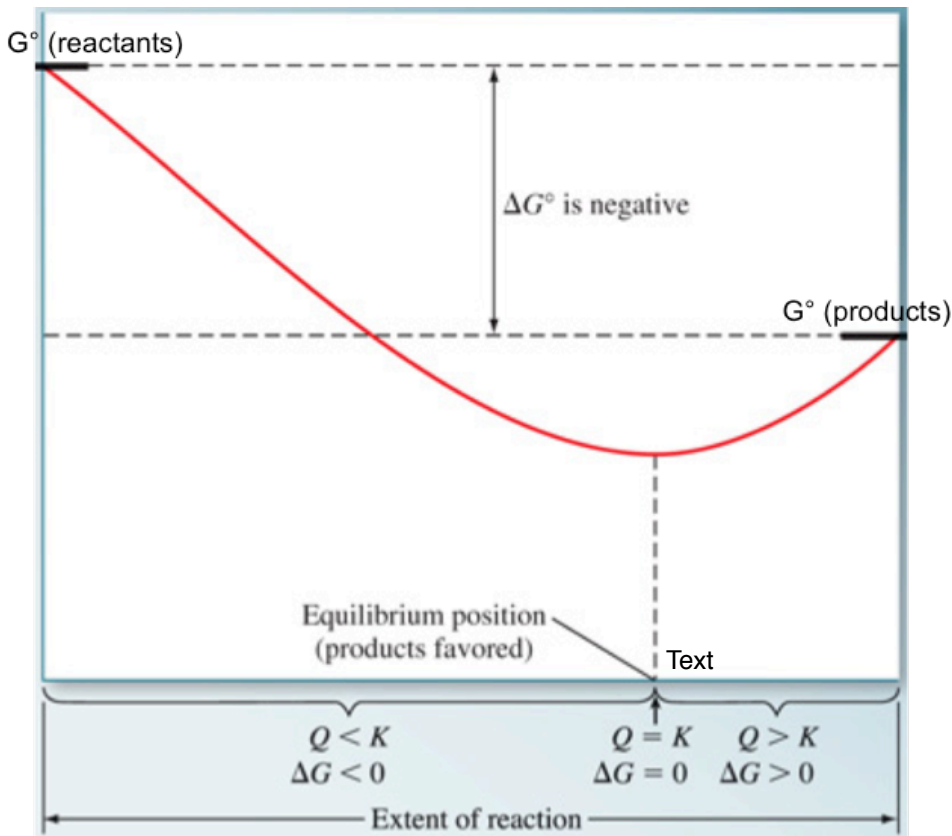
Solution:

The reaction quotient is  $Q = (1.75)^2 / (5.25) = 0.583$

$$\begin{aligned} \Delta G &= 2.60 \text{ kJ/mol} + (8.314 \times 10^{-3} \text{ kJ mol}^{-1}\text{K}^{-1})(298 \text{ K})(-0.539) \\ &= 1.26 \text{ kJ/mol.} \end{aligned}$$

The reaction will thus run backwards spontaneously.

## Free energy diagram (free energy vs reaction coordinate)



$$\Delta G^\circ = G^\circ_{\text{products}} - G^\circ_{\text{reactants}}$$

- from tables
- changes with  $T$

Lowest point is equilibrium

$\Delta G$  is the slope at any point

Can approach equilibrium from either side ( $Q$  vs  $K$ )

$\Delta G$  tells us the direction the reaction needs to proceed to achieve equilibrium

$\Delta G^\circ$  tells us the position of equilibrium ( $K$ )

Large  $|\Delta G^\circ|$  means the equilibrium lies further to the reactant or product side

