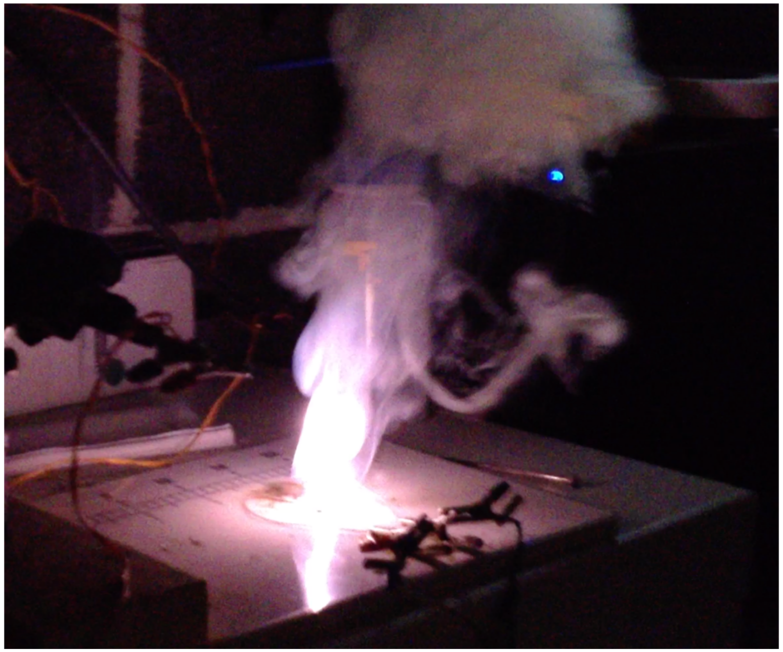
# Chapter 18

# Thermodynamics



# Thermodynamics

## Study of Energy Changes During Observed Processes

$\Delta$ = change

**Enthalpy (H):** Energy of reaction, often described in terms of heat (CHM 101)

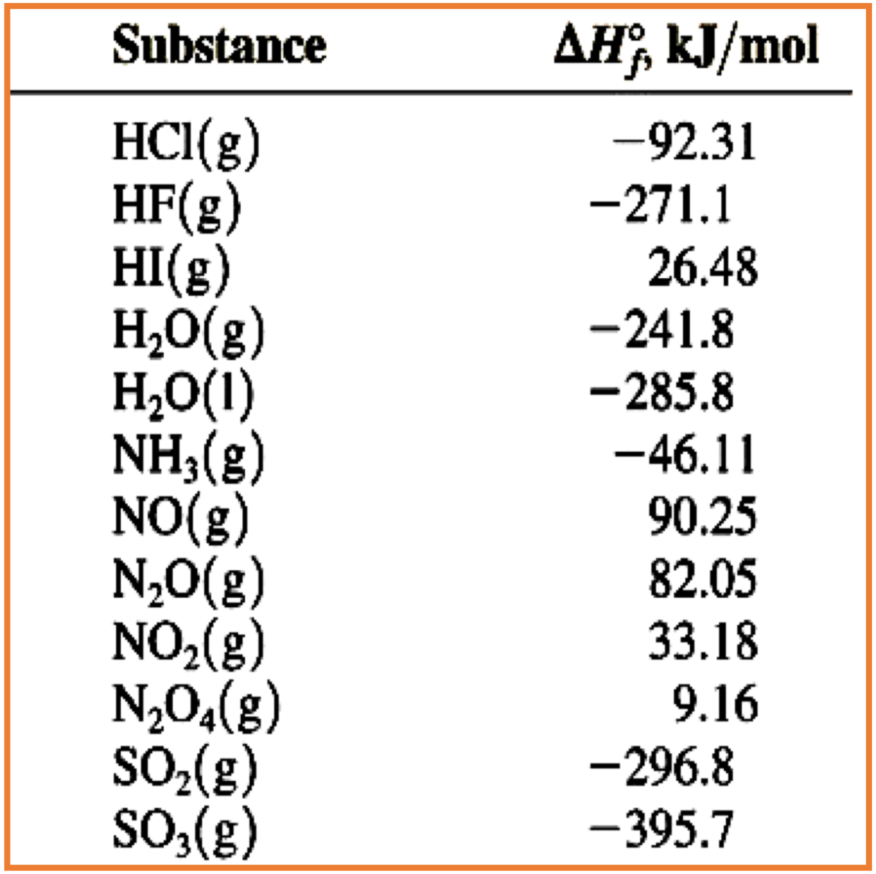
**Entropy (S):** Measurement of disorder

**Free Energy (G):**

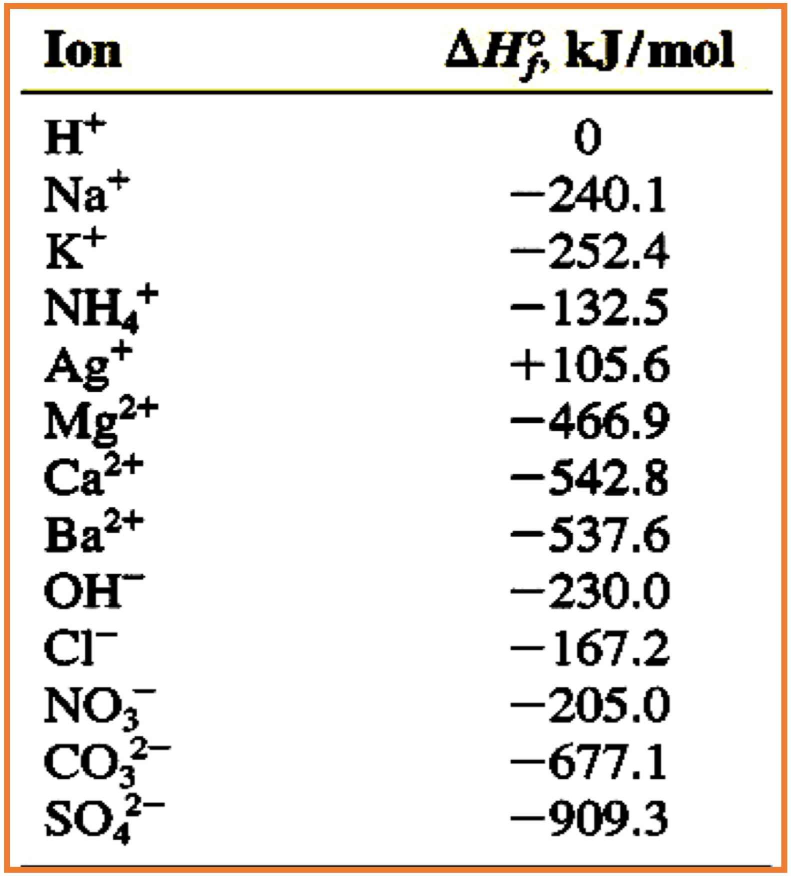
- Used to predict whether a process will occur spontaneously
- Spontaneously = without assistance
- Depends on enthalpy, entropy, and temperature

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

# Some Enthalpies of Formation at 25˚C



| Substance | $\Delta H_f^\circ$, kJ/mol |
|---|---|
| $HCl(g)$ | −92.31 |
| $HF(g)$ | −271.1 |
| $HI(g)$ | 26.48 |
| $H_2O(g)$ | −241.8 |
| $H_2O(l)$ | −285.8 |
| $NH_3(g)$ | −46.11 |
| $NO(g)$ | 90.25 |
| $N_2O(g)$ | 82.05 |
| $NO_2(g)$ | 33.18 |
| $N_2O_4(g)$ | 9.16 |
| $SO_2(g)$ | −296.8 |
| $SO_3(g)$ | −395.7 |



| Ion | $\Delta H_f^\circ$, kJ/mol |
|---|---|
| $H^+$ | 0 |
| $Na^+$ | −240.1 |
| $K^+$ | −252.4 |
| $NH_4^+$ | −132.5 |
| $Ag^+$ | +105.6 |
| $Mg^{2+}$ | −466.9 |
| $Ca^{2+}$ | −542.8 |
| $Ba^{2+}$ | −537.6 |
| $OH^-$ | −230.0 |
| $Cl^-$ | −167.2 |
| $NO_3^-$ | −205.0 |
| $CO_3^{2-}$ | −677.1 |
| $SO_4^{2-}$ | −909.3 |

All $\Delta H_f$ are for standard conditions
25˚C, 1 atm, 1M aqueous solution, 1 mole product

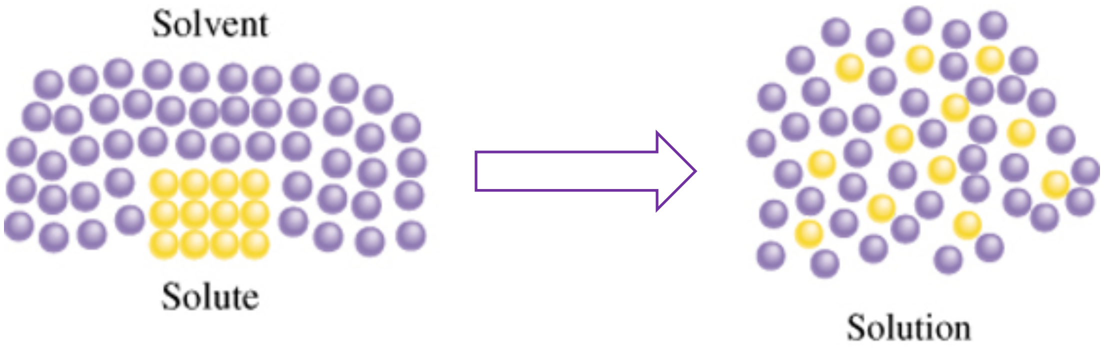
# Three Laws of Thermodynamics

## First Law of Thermodynamics:

- Energy cannot be created or destroyed
- The total energy of the Universe must be constant
- Energy can be converted from one form to another, or transferred between systems & surroundings

## Second Law of Thermodynamics:

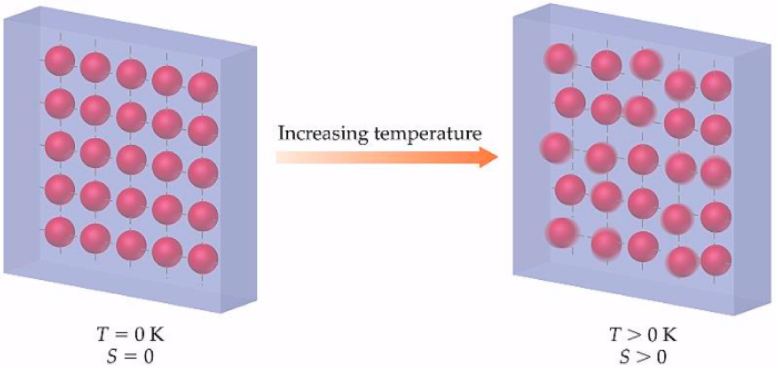
- The entropy of the Universe ($\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$) increases for spontaneous processes
- For spontaneous (irreversible) processes: $\Delta S_{univ} > 0$
- For reversible processes: $\Delta S_{univ} = 0$



# Three Laws of Thermodynamics

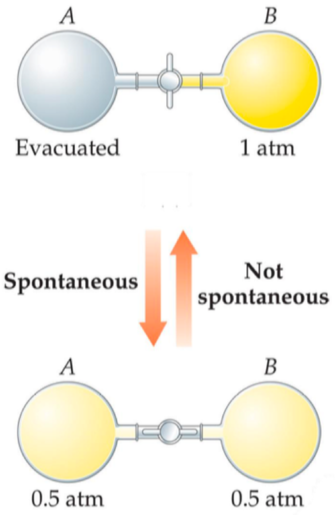
## Third Law of Thermodynamics:

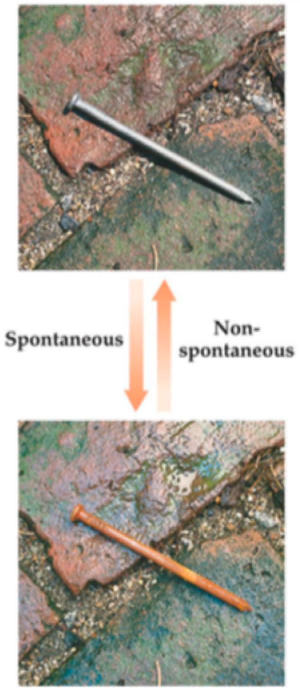
- The entropy of a pure crystalline substance at absolute zero (0K) is zero.
- Scientists have come close to absolute zero, but 0K has not yet been achieved
- At 0K there is absolutely no molecular movement
- Provides a starting point for determining ΔS
  - Start as close to 0K as possible, warm material up to a specific temperature and calculate ΔH
  - $S = \Delta H/T$
  - Note: Since S is temp. dependent, to use this equation the process must be isothermal.



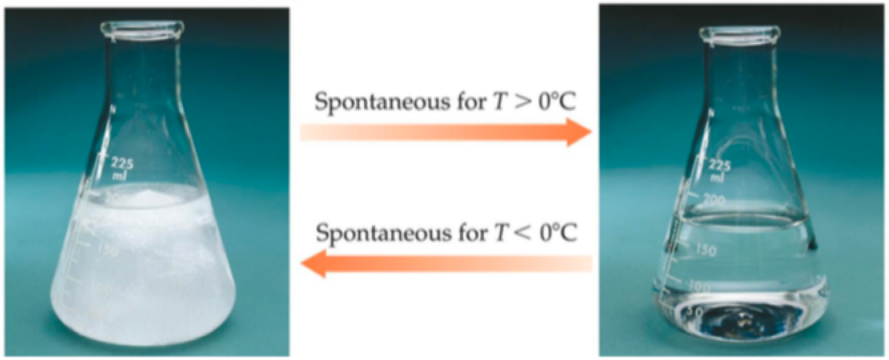
# Spontaneous Processes

- Processes that are spontaneous in one direction are non-spontaneous in the other direction.
- Spontaneous processes can be fast (e.g. explosion) or slow (e.g. rusting)
- Spontaneity generally temperature dependent
  - > 0˚C, ice melting is spontaneous
  - < 0˚C, ice freezing is spontaneous





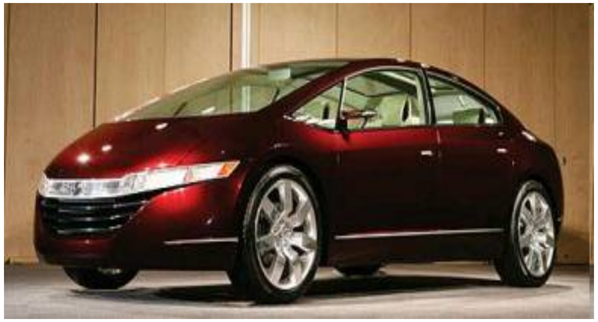
Water flows naturally downhill but must be pumped uphill



# Enthalpy & Spontaneity

## Reaction of $H_2$ & $O_2$ to from $H_2O$

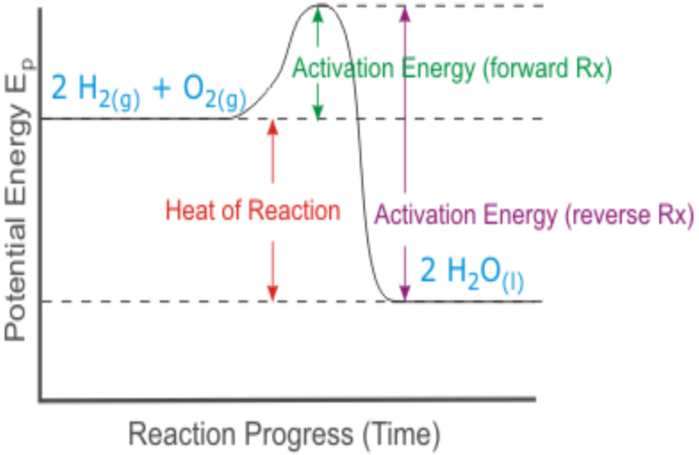
- Used in fuel cells
- Exothermic reaction
- $\Delta H = -286$ kJ/mol
- Favors $H_2O$ production



$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$$

## Reality at room temp:

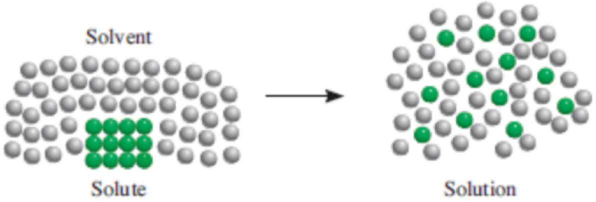
- Not a spontaneous reaction
- $H_2$ & $O_2$ remain unreacted
- No water is formed without added energy to initiate
- $E_{act} = +112$kJ/mol – too high



**Enthalpy determines the equilibrium state, but enthalpy alone does NOT determine spontaneity**

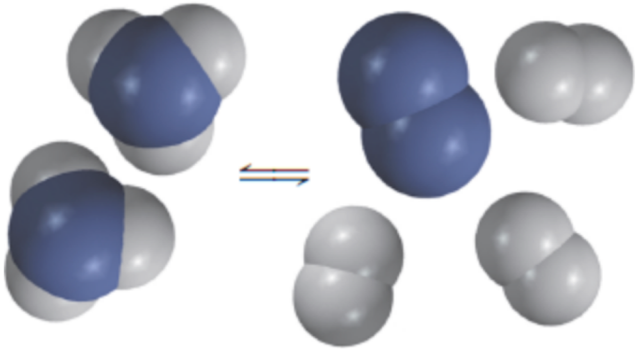
**Also need to consider entropy**

# Entropy (S)



**Entropy is defined as a measure of the randomness or disorder of a system**

- It is related to the various modes of motion in molecules (or of ions/atoms)
- Entropy is a state function (like enthalpy & total energy)
  - State functions are defined by final-initial conditions (independent of process)
  - $\Delta S = S_{final} - S_{initial}$
- Entropy is increased when, for example:
  - Moles of products > moles of reactants
  - More complex molecules are broken down into smaller, simpler molecules
  - There is a phase change to a more disordered phase (disorder: gas>liquid>solid)



# Spontaneous Processes

Which of the following processes are spontaneous?

(a) Separating a mixture of $N_2$ and $O_2$ into two separate samples

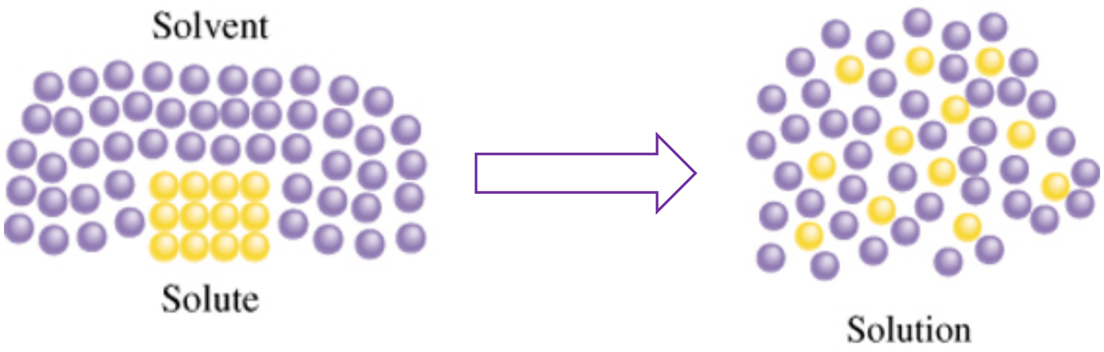
(b) Alignment of iron filings in a magnetic field

(c) Dissolution of HCl(g) in water to form HCl(aq)

(d) Sublimation of $CO_2$(s) at -100˚C, 1 atm ($CO_2$ sublimation point is -78˚C, 1 atm)

(e) Reaction of copper with oxygen to form CuO under typical environmental conditions in RI.

# Entropy & Solvation



**Generally, dissolving a solute in a solvent <u>increases</u> entropy**

<u>However</u>:

When solutes are dissolved, the water molecules around them have less ability to move due to interactions with the solute (H-bonds, ion-dipole interactions, etc.).

In some cases (especially with large ions) this may result in an overall decrease in entropy.

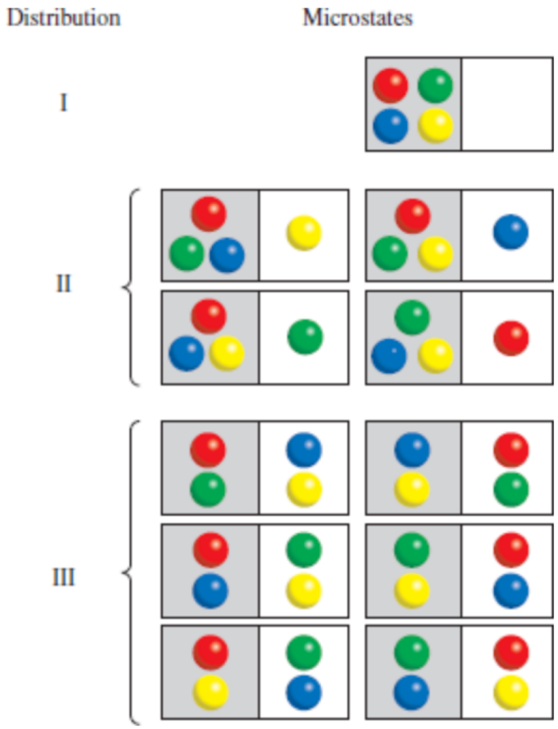
# Entropy & Microstates

Entropy is related to the number of "microstates" through the equation:

$$S = k \ln W$$

k = Boltzmann constant ($1.38\times10^{-23}$ J/K)

W = # microstates.



$\Delta S = S_f - S_i$

$= k \ln W_f - k \ln W_i$

$= k \ln (W_f/W_i)$

Microstate is a term used to describe the number of ways that a given state can be achieved.

**More possible variation = More microstates = Higher S**

# Predicting Entropy Changes

Indicate whether the following produces an increase or decrease in the entropy of the system:

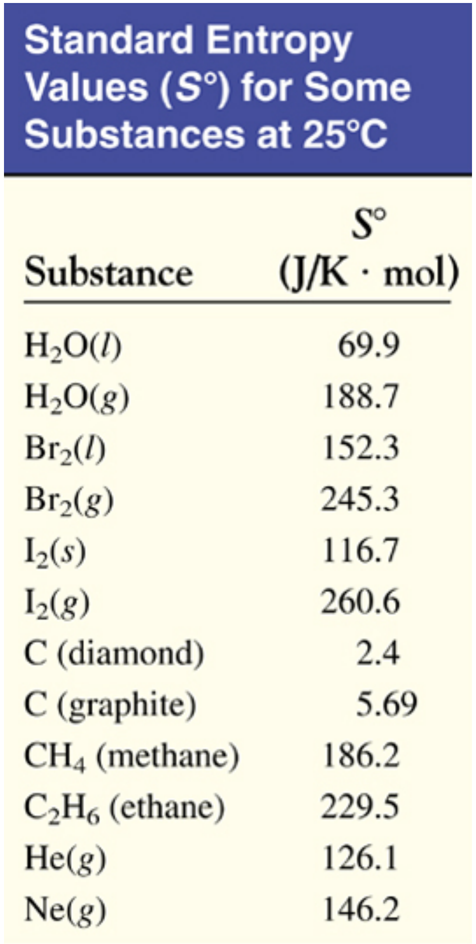
(a) $CO_2(s) \rightarrow CO_2(g)$

(b) $CaO(s) + CO_2(g) \rightarrow CaCO_3(s)$

(c) $NH_4Cl(s) \rightarrow HCl(g) + NH_3(g)$

(d) $NaCl(s) \xrightarrow{H_2O} NaCl(aq)$

# Some Standard Molar Entropy Values (larger table in Appendix 2 of Textbook)



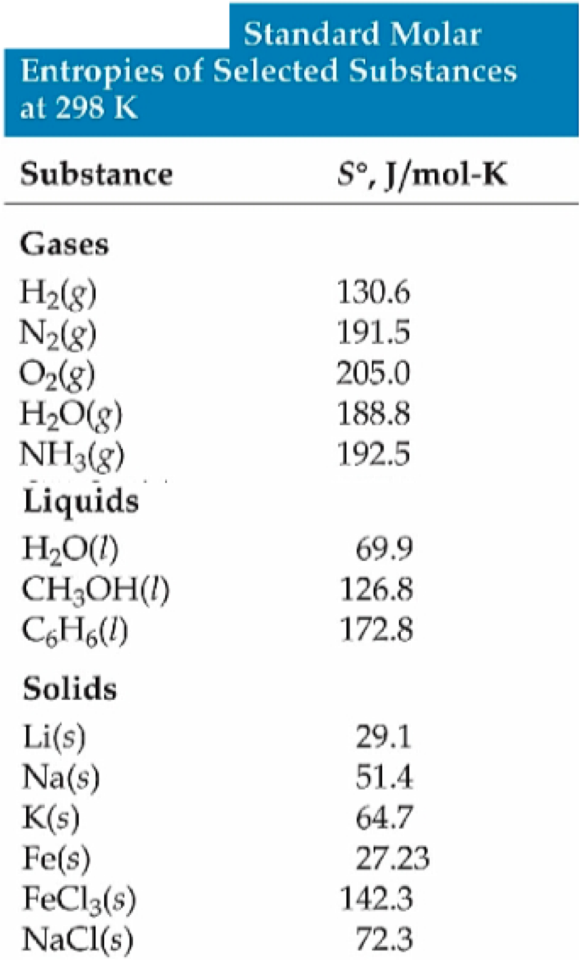
**Standard Entropy Values ($S°$) for Some Substances at 25°C**

| Substance | $S°$ (J/K · mol) |
|---|---|
| $H_2O(l)$ | 69.9 |
| $H_2O(g)$ | 188.7 |
| $Br_2(l)$ | 152.3 |
| $Br_2(g)$ | 245.3 |
| $I_2(s)$ | 116.7 |
| $I_2(g)$ | 260.6 |
| C (diamond) | 2.4 |
| C (graphite) | 5.69 |
| $CH_4$ (methane) | 186.2 |
| $C_2H_6$ (ethane) | 229.5 |
| $He(g)$ | 126.1 |
| $Ne(g)$ | 146.2 |

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

For similar molecules, $S^\circ$ tends to increase with:

- Increasing molar mass
- Increased number of atoms in formula



**Standard Molar Entropies of Selected Substances at 298 K**

| Substance | $S°$, J/mol-K |
|---|---|
| **Gases** | |
| $H_2(g)$ | 130.6 |
| $N_2(g)$ | 191.5 |
| $O_2(g)$ | 205.0 |
| $H_2O(g)$ | 188.8 |
| $NH_3(g)$ | 192.5 |
| **Liquids** | |
| $H_2O(l)$ | 69.9 |
| $CH_3OH(l)$ | 126.8 |
| $C_6H_6(l)$ | 172.8 |
| **Solids** | |
| $Li(s)$ | 29.1 |
| $Na(s)$ | 51.4 |
| $K(s)$ | 64.7 |
| $Fe(s)$ | 27.23 |
| $FeCl_3(s)$ | 142.3 |
| $NaCl(s)$ | 72.3 |

# CHM 101 Review: Calculating Reaction Enthalpy from Standard Enthalpies of Formation

$\Delta H_{reaction} = \Sigma\Delta H_{products} - \Sigma\Delta H_{reactants}$ (Σ = sum)

$C_2H_5OH(l) + 3\ O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$

- **$\Delta H_f^\circ$ Reactants:**
- $C_2H_5OH$ (l): -277.7 kJ/mol x 1 = -277.7 kJ/mol
- $O_2$: 0.0 kJ/mol x 3 = 0.0 kJ/mol
- Total reactants = -277.7kJ/mol + 0.0kJ/mol = -277.7kJ/mol
- **$\Delta H_f^\circ$ Products**
- $CO_2(g)$: -393.5 kJ/mol x 2 = -787.0kJ/mol
- $H_2O(l)$: -285.8 kJ/mol x 3 = -857.4kJ/mol
- Total products = -787.0kJ/mol + -857.4kJ/mol = -1644.4kJ/mol
- **$\Delta H^\circ = \Sigma\Delta H_{products} - \Sigma\Delta H_{reactants}$**

  = -1644.4kJ/mol – (-277.7kJ/mol) = **-1366.7kJ/mol**

# Calculating Reaction Entropy from Standard Entropies

$\Delta S_{reaction} = \Sigma S°_{products} - \Sigma S°_{reactants}$ (Σ = sum)

$C_2H_5OH(l) + 3\ O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$

**S° Reactants:**

- $C_2H_5OH$ (l): 161.2 J/mol K x 1 = 161.2 J/mol K
- $O_2$: 205.0 J/mol K x 3 = 615.0 J/mol K
- Total reactants = 161.2 J/mol K + 615.0 J/mol K=776.2 J/mol K

**S° Products**

- $CO_2(g)$: 213.6 J/mol K x 2 = 427.2 J/mol K
- $H_2O(l)$: 69.9 J/mol K x 3 = 209.7 J/mol K
- Total products = 427.2 J/mol K + 209.7 J/mol K =636.9 J/mol K

$\Delta S° = \Sigma S_{products} - \Sigma S_{reactants}$

= 636.9 J/mol K – 776.2 J/mol K) = **-139.3 J/mol K**

# Calculating Reaction Entropy from Standard Entropies

1. What is the molar change in entropy for water freezing at 25˚C? A: -28.9 J/mol K

2. What is the standard entropy change for the following reaction? A: 178.7 J/mol K

$$Al_2O_3\,(s) + 3H_2(g) \rightarrow 2\,Al(s) + 3H_2O(g)$$

# Calculating Entropy (S) from ΔH

The normal boiling point of ethanol ($C_2H_5OH$, 46.07g/mol) is 78.3˚C and its molar enthalpy of vaporization is 38.56 kJ/mol.  What is the change in entropy in the system when 68.3g of gaseous ethanol at 1 atm condenses to liquid at the normal boiling point? A: -163 J/K

# Phase Changes & Entropy

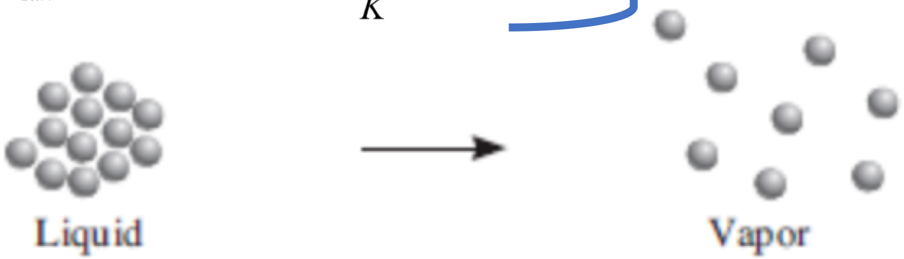
## Less Order = Greater Entropy

$$\Delta S_{sys} = \frac{q_{rev}}{T} = \frac{(1mol)(6.01x10^3\,J/mol)}{273K} = 22.0\frac{J}{K}$$

$$\Delta S_{surr} = \frac{q_{rev}}{T} = \frac{(1mol)(-6.01x10^3\,J/mol)}{310K} = -19.4\frac{J}{K}$$

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} = 22.0 - 19.4 = 2.6\frac{J}{K}$$

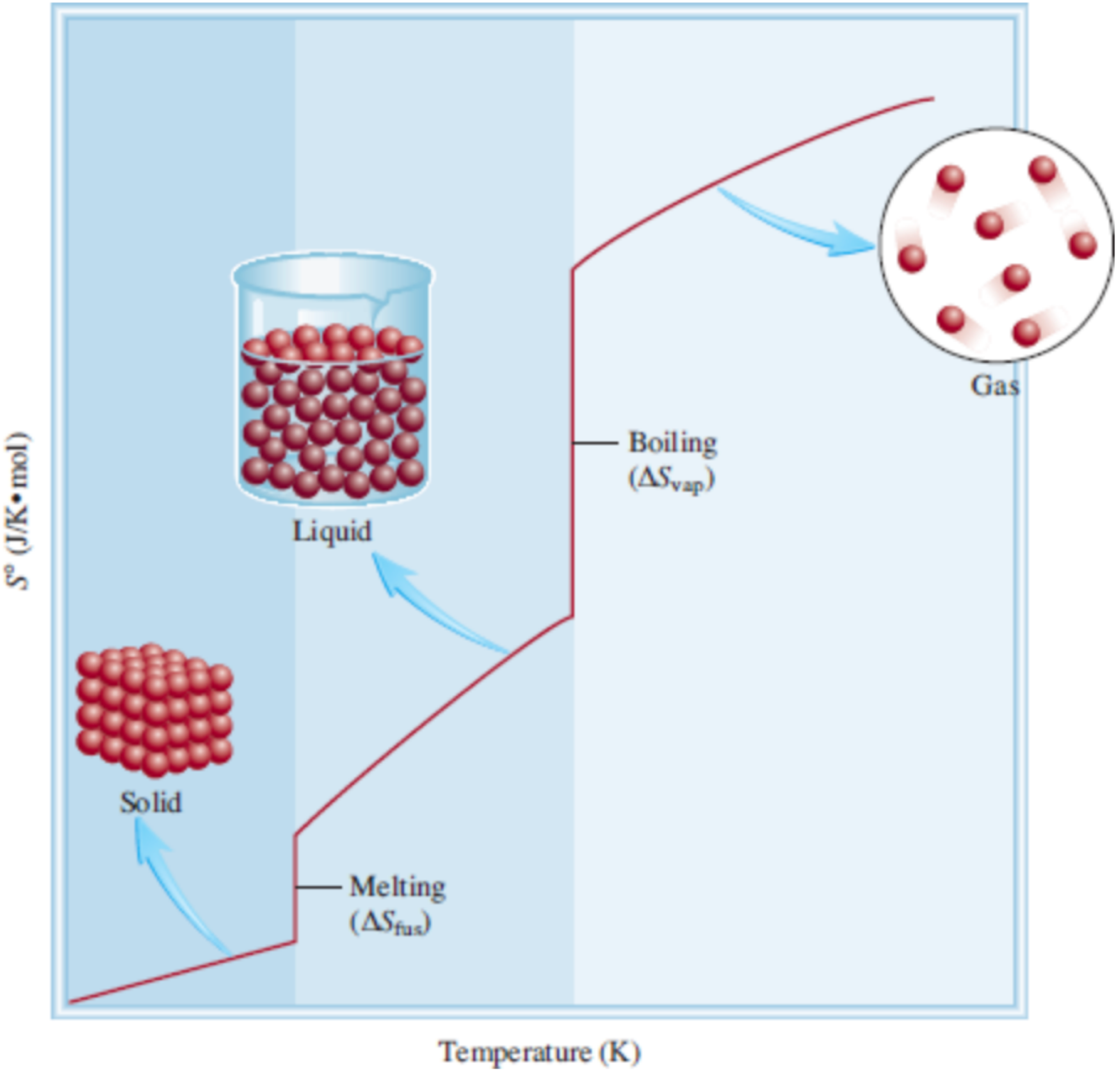
ΔS calculation for melting ice in the palm of your hand



Melting & Vaporization are favored by entropy

Freezing & Condensation (exothermic) are favored by enthalpy

What determines which process will occur?



# Spontaneity is Temperature Dependent!

# Gibbs Free Energy (G)

**The maximum useful work that can be done by a system on its surroundings in a spontaneous process at constant T & P.**

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

The equation comes from thermodynamic principles

Eq1: $\Delta S^{\circ}_{univ} = S^{\circ}_{surr} + S^{\circ}_{sys}$

Eq2: $\Delta S_{surr} = -\Delta H_{sys}/T$

Substitute Eq2 for $S^{\circ}_{surr}$

$$\Delta S^{\circ}_{univ} = (-\Delta H_{sys}/T) + S^{\circ}_{sys}$$

Multiply by –T to get

$$-T\Delta S^{\circ}_{univ} = \Delta H_{sys} - T\Delta S_{sys}$$

Let $-T\Delta S^{\circ}_{univ} = \Delta G$ to get

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

# Standard Free Energy, $\Delta G^\circ$

**Free energy change when reactants and products are in their standard states**

(pure material, 1 atm, 1M if in solution, zero for elements in standard state)

$$\Delta G^\circ_{reaction} = \Sigma G_f^\circ{}_{products} - \Sigma G_f^\circ{}_{reactants}$$

# Gibbs Free Energy & Spontaneity

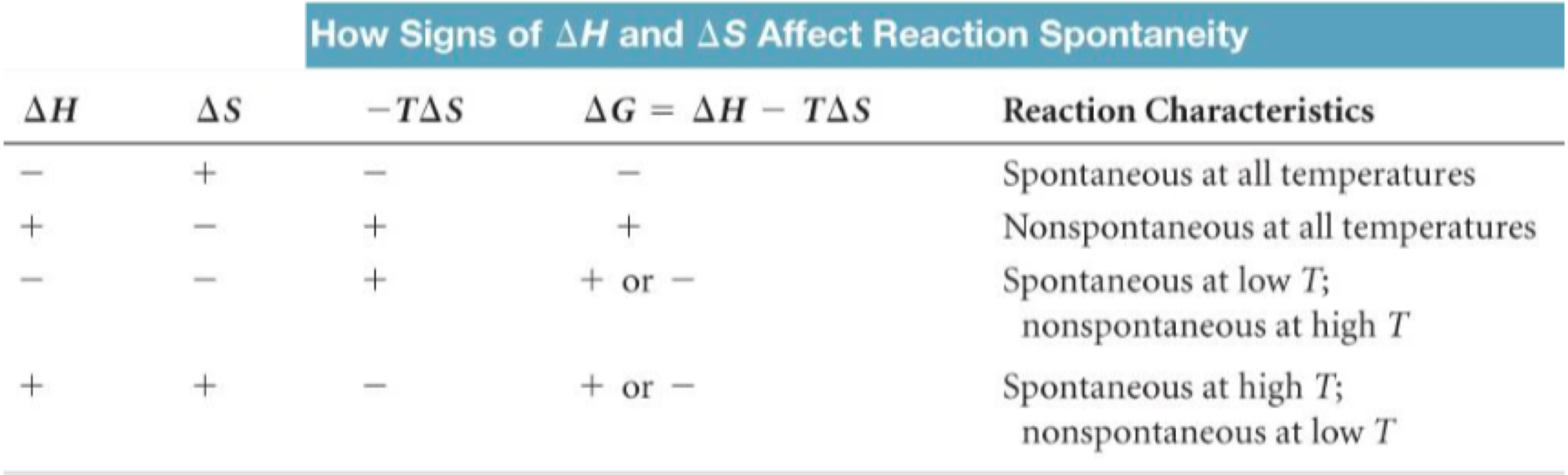
$\Delta G < 0$ (negative), the process is spontaneous

$\Delta G > 0$ (positive), the process is non-spontaneous

$\Delta G = 0$ the process is at equilibrium

| **$\Delta H$** | **$\Delta S$** | **$\Delta G$** | **Spontaneous?** |
|---|---|---|---|
| negative | positive | negative | yes |
| positive | negative | positive | no |
| negative | negative | ? | Temp Dependent |
| positive | positive | ? | Temp Dependent |

# Gibbs Free Energy & Spontaneity



**How Signs of $\Delta H$ and $\Delta S$ Affect Reaction Spontaneity**

| $\Delta H$ | $\Delta S$ | $-T\Delta S$ | $\Delta G = \Delta H - T\Delta S$ | Reaction Characteristics |
|---|---|---|---|---|
| − | + | − | − | Spontaneous at all temperatures |
| + | − | + | + | Nonspontaneous at all temperatures |
| − | − | + | + or − | Spontaneous at low *T*;<br>nonspontaneous at high *T* |
| + | + | − | + or − | Spontaneous at high *T*;<br>nonspontaneous at low *T* |

# Gibbs Free Energy & Spontaneity

1. A certain reaction has $\Delta H^\circ = -19.5\text{kJ}$ and $\Delta S^\circ = 42.7\text{J/K}$.

(a) Is the reaction exothermic or endothermic? A: exothermic

(b) Does the reaction lead to an increase or decrease in the randomness or disorder of the system? A: increase

(c) Calculate $\Delta G^\circ$ at 298K A: -32.2kJ

(d) Is the reaction spontaneous at 298K under standard conditions? A: yes

2. Is the following process spontaneous at 25˚C? at 75˚C?

$Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$ A: no

## Step 1: Calculate ΔH

## Step 2: Calculate ΔS

## Step 3: Calculate ΔG

3. At what temperature will the following process become spontaneous?

$$Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$$

A: -200˚C

# Free Energy & Equilibrium

During a reaction, not all of the reactants and products will be in their standard state. Under any conditions (standard or nonstandard), the free energy change is:

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$R = 8.314\times10^{-3}$ kJ/mol K
T = temperature in K
Q = reaction quotient

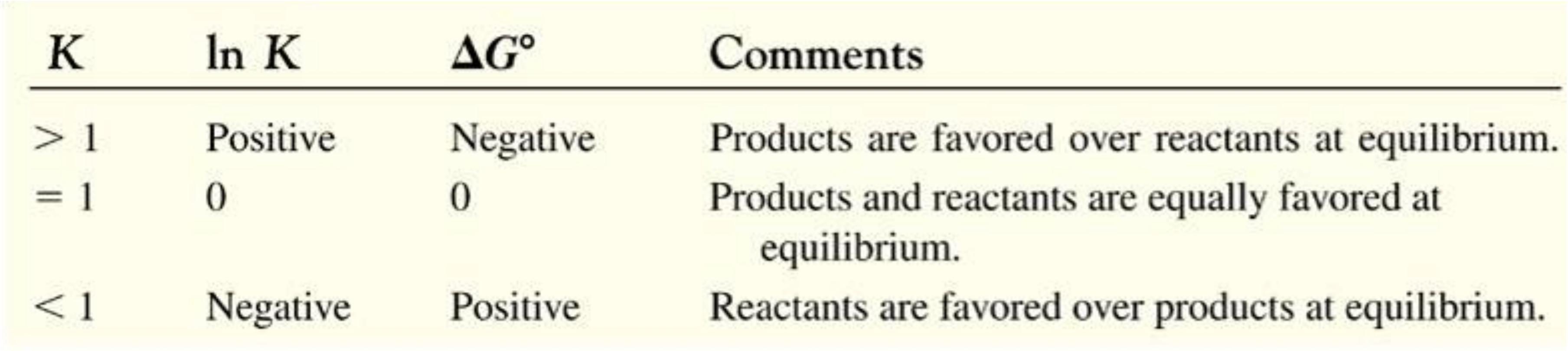
(Under standard conditions, all concentrations are 1M, so Q = 1, $\ln Q = 0$, and $\Delta G = \Delta G^\circ$)

At equilibrium: $\Delta G = 0$ and $Q = K$ (K is equilibrium constant)

So the equation becomes: $0 = \Delta G^\circ + RT \ln K$

Therefore, at equilibrium: $\boldsymbol{\Delta G^\circ = -RT \ln K}$

# Free Energy & Equilibrium



| $K$ | $\ln K$ | $\Delta G°$ | Comments |
|---|---|---|---|
| $> 1$ | Positive | Negative | Products are favored over reactants at equilibrium. |
| $= 1$ | 0 | 0 | Products and reactants are equally favored at equilibrium. |
| $< 1$ | Negative | Positive | Reactants are favored over products at equilibrium. |

$\Delta G^\circ < 0$ (negative), the forward reaction is spontaneous

$\Delta G^\circ > 0$ (positive), the reverse reaction is spontaneous

$\Delta G^\circ = 0$ the reaction is at equilibrium

The magnitude of $\Delta G^\circ$ indicates how far the standard state is from equilibrium
(more negative $\Delta G^\circ$ = larger K)

# Free Energy & Equilibrium

1. Calculate ΔG° for the following reaction at 25°C.

$$Fe(OH)_2(s) \rightleftharpoons Fe^{2+}(aq) + 2OH^{-}(aq)$$

$K_{sp}$ for $Fe(OH)_2$ is $1.6 \times 10^{-14}$

A: 79kJ/mol

2. For the following reaction:

A: (a) -5.41 kJ/mol
(b) 0.295 kJ/mol

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

(a) Using data from Appendix 2, calculate **Δ**G° at 298K
(b) Calculate **Δ**G at 298K if the partial pressure of $NO_2$ and $N_2O_4$ are 0.40atm and 1.60atm, respectively.

# 3. Compare the molar solubility of lead chloride at 25˚C and 90˚C.

$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^{-}(aq)$

$K_{sp}$ for $PbCl_2$ is $1.6 \times 10^{-5}$ at 25˚C

From Table:

| **$\Delta H^\circ_f$ (kJ/mol)** | **$S^\circ$ (J/molK)** |
|---|---|
| $PbCl_2(s) = -359$ | $PbCl_2(s) = 136$ |
| $Pb^{2+}(aq) = -1.7$ | $Pb^{2+}(aq) = 10.5$ |
| $Cl^{-}(aq) = -167.2$ | $Cl^{-}(aq) = 56.5$ |

A: solubility at 90˚C about double the solubility at 25˚C