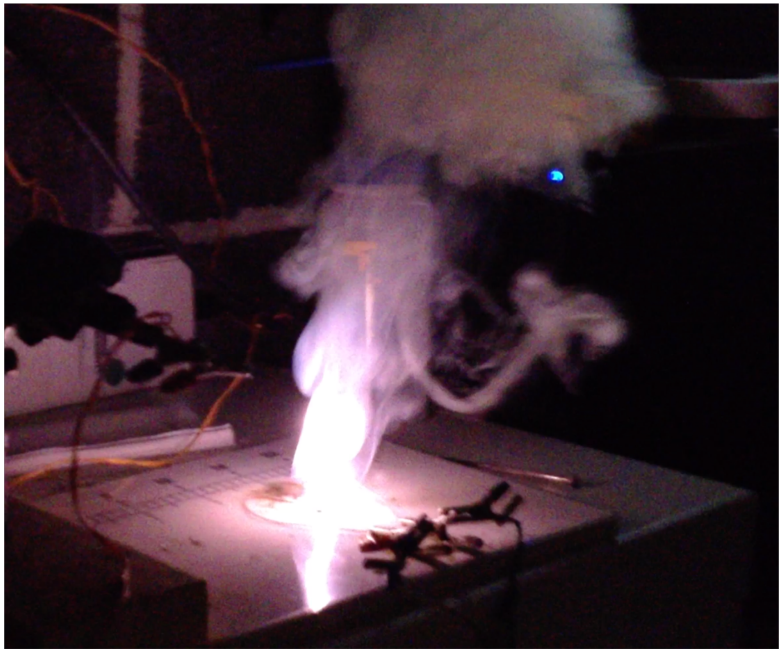
Chapter 18

Thermodynamics



Thermodynamics

Study of Energy Changes During Observed Processes

Δ = change

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

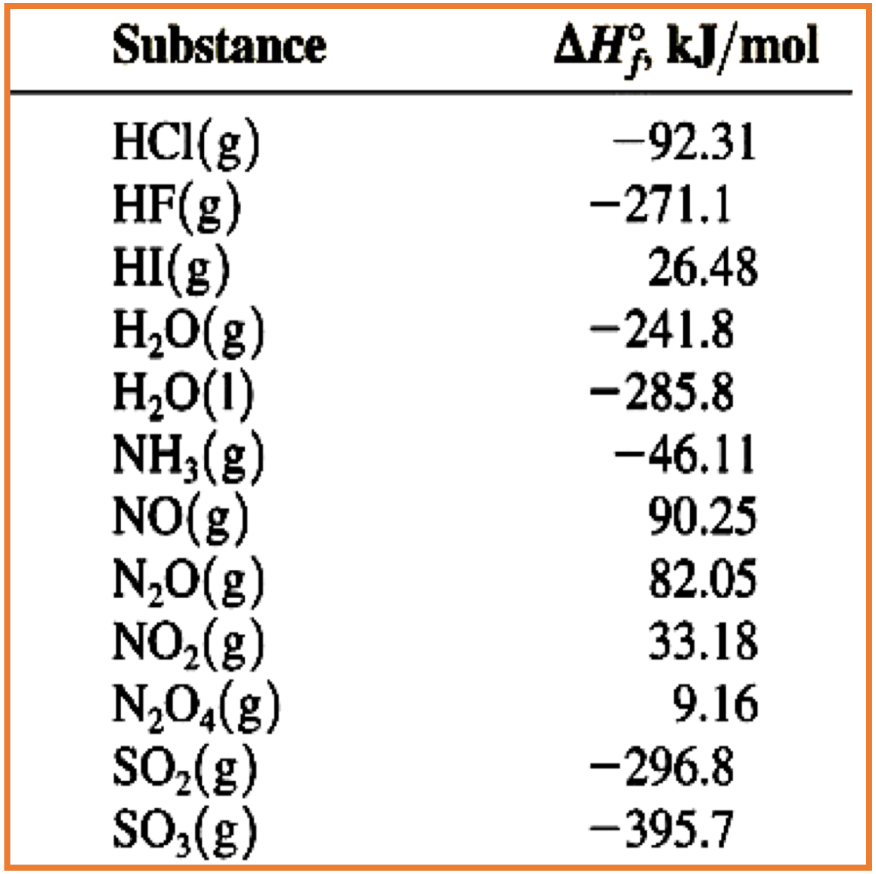
Entropy (S): Measurement of disorder

Free Energy (G):

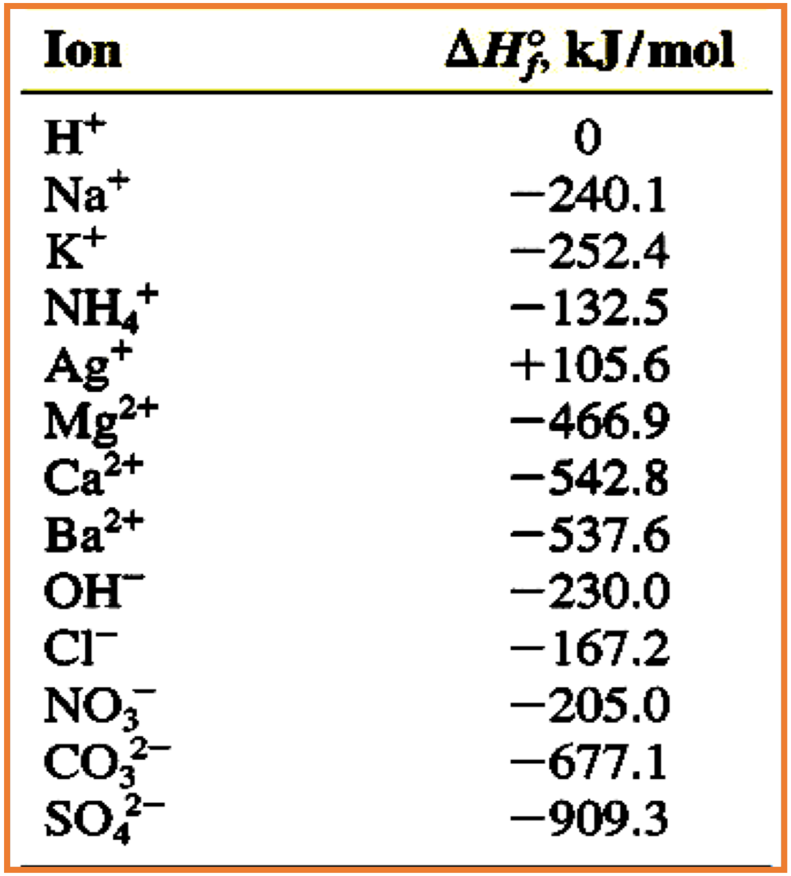
- Used to predict whether a process will occur spontaneously
- Spontaneously = without assistance
- Depends on enthalpy, entropy, and temperature

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

Some Enthalpies of Formation at 25˚C



Substance	ΔH_f°, 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	ΔH_f°, 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 ΔH_f are for standard conditions
25˚C, 1 atm, 1M aqueous solution, 1 mole product

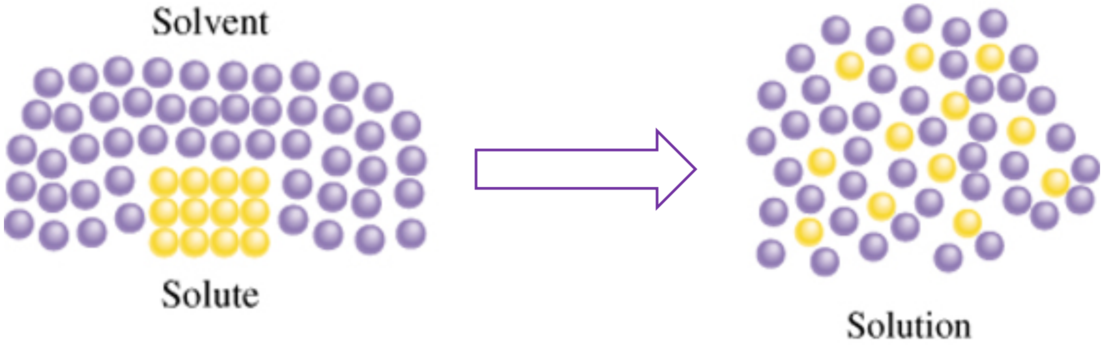
Three Laws of Thermodynamics

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:

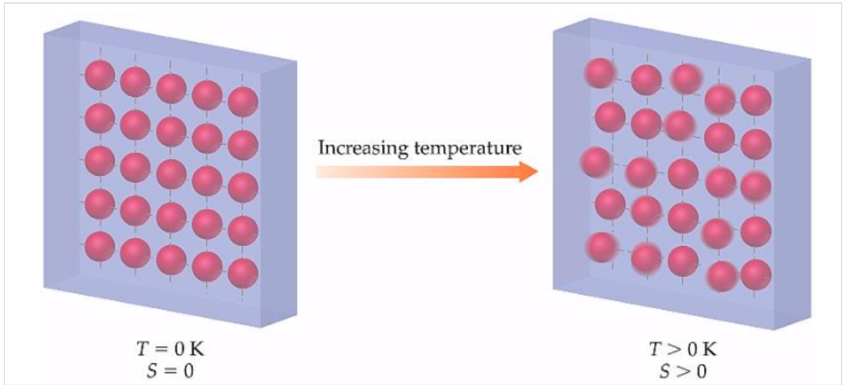
- The entropy of the Universe ($\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$) increases for spontaneous processes
- For spontaneous (irreversible) processes: $\Delta S_{univ} > 0$
- For reversible processes: $\Delta S_{univ} = 0$



Three Laws of Thermodynamics

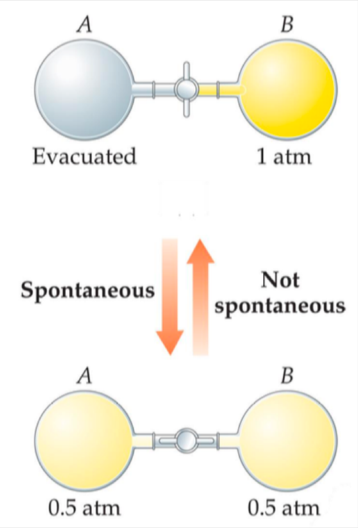
Third Law of Thermodynamics:

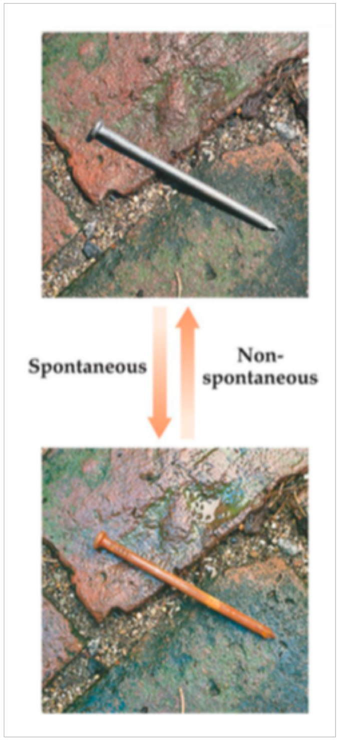
- The entropy of a pure crystalline substance at absolute zero (0K) is zero.
- Scientists have come close to absolute zero, but 0K has not yet been achieved
- At 0K there is absolutely no molecular movement
- Provides a starting point for determining ΔS
  - Start as close to 0K as possible, warm material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



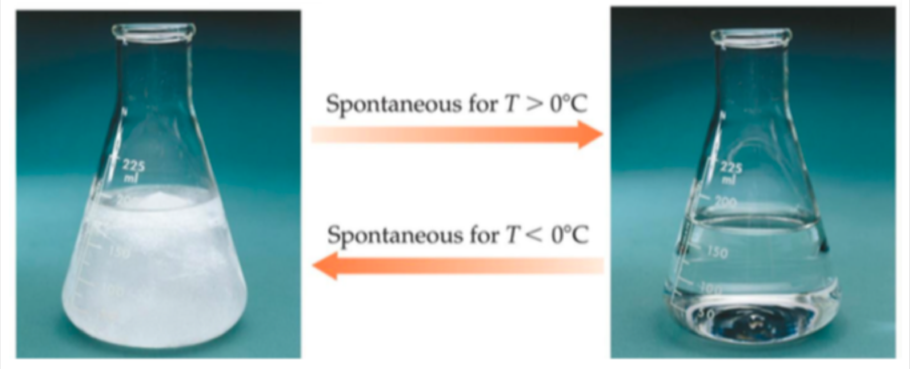
Spontaneous Processes

- 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





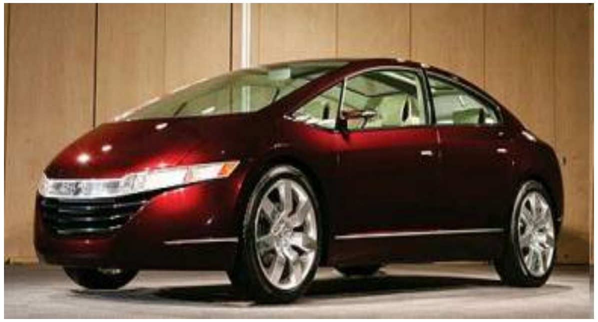
Water flows naturally downhill but must be pumped uphill



Enthalpy & Spontaneity

Reaction of H_2 & O_2 to from H_2O

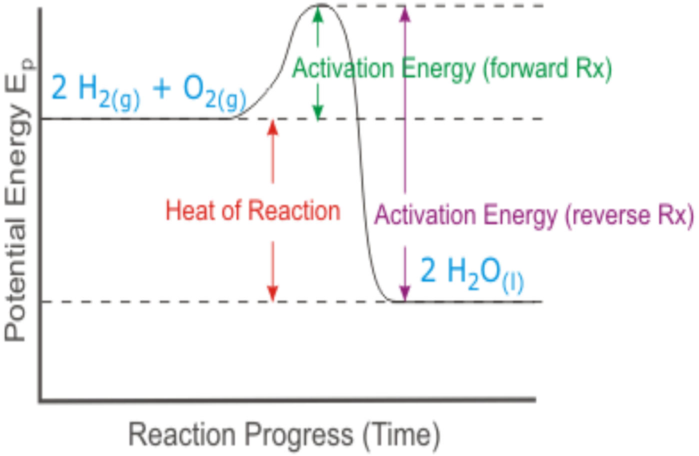
- Used in fuel cells
- Exothermic reaction
- ΔH = -286 kJ/mol
- Favors H_2O production



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

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} = +112kJ/mol – too high



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

Also need to consider entropy

Spontaneous Processes

Which of the following processes are spontaneous?

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

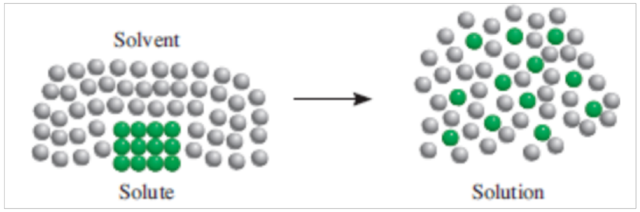
(b) Alignment of iron filings in a magnetic field

(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)

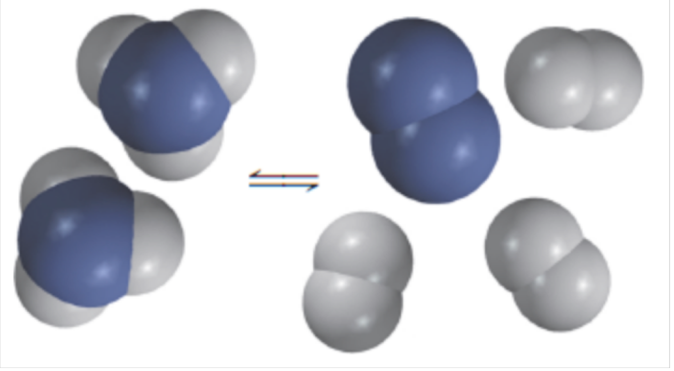
(e) Reaction of copper with oxygen to form CuO under typical environmental conditions in RI.

Entropy (S)

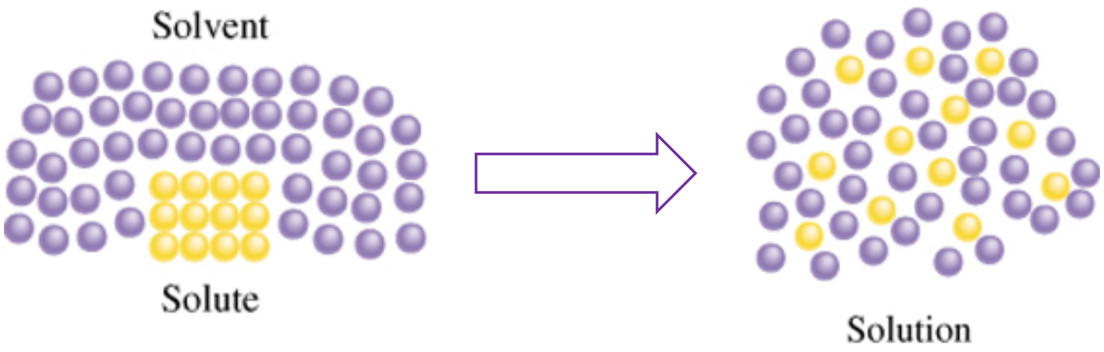


Entropy is defined as a measure of the randomness or disorder of a system

- 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)



Entropy & Solvation



Generally, dissolving a solute in a solvent increases entropy

However:

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:

$$S = k \ln W$$

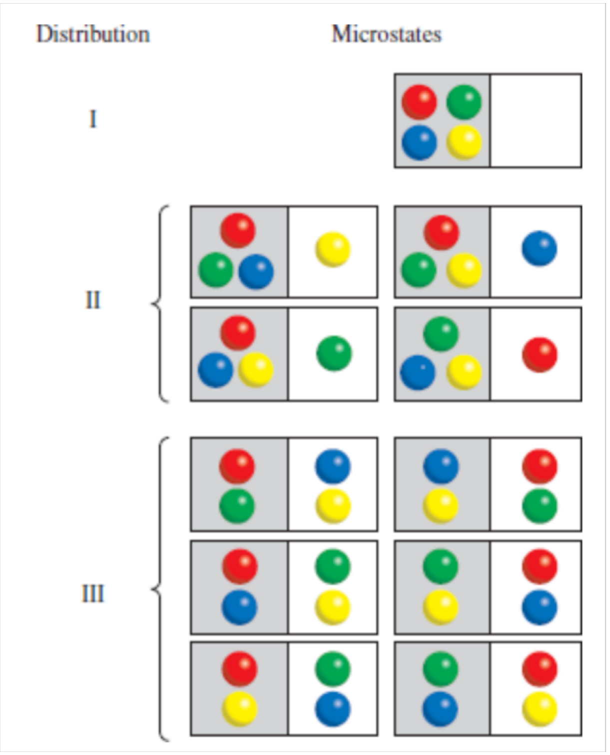
k = Boltzmann constant (1.38×10^{-23} J/K)

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:

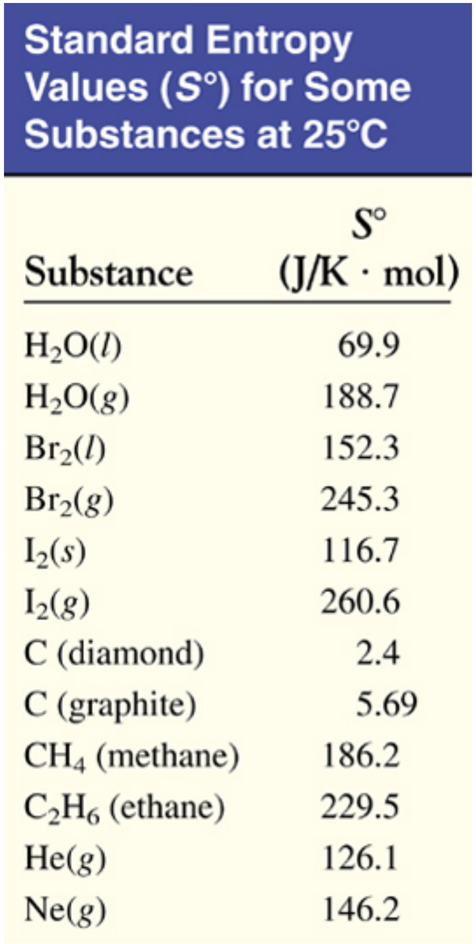
(a) $CO_2(s) \rightarrow CO_2(g)$

(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)



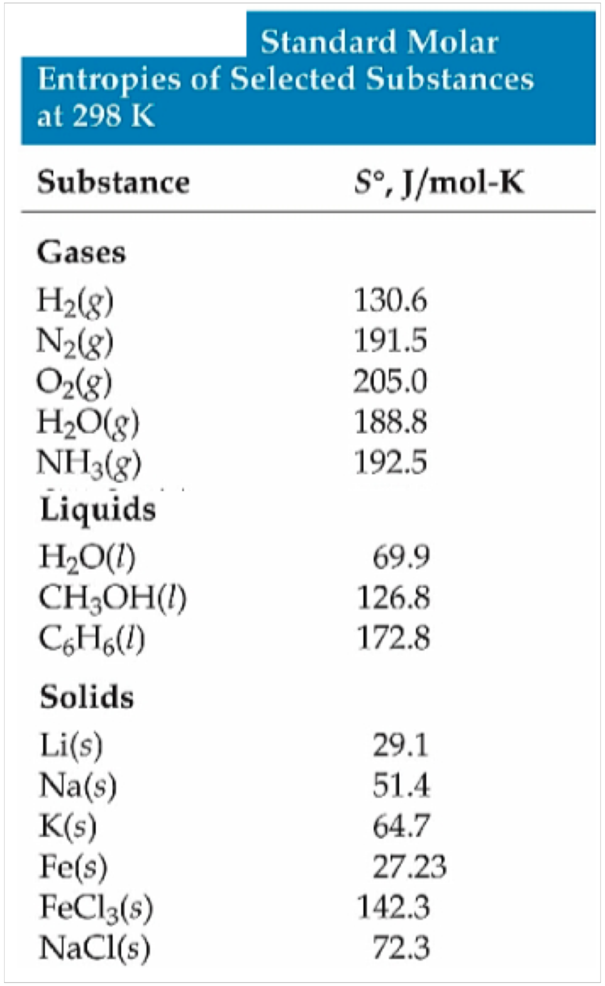
Standard Entropy Values ($S°$) for Some Substances at 25°C

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

$S°_{gas} > S°_{liquid} > S°_{solid}$

For similar molecules, S° 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)

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

- **ΔH_f° 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
- **ΔH_f° 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

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

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

= 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

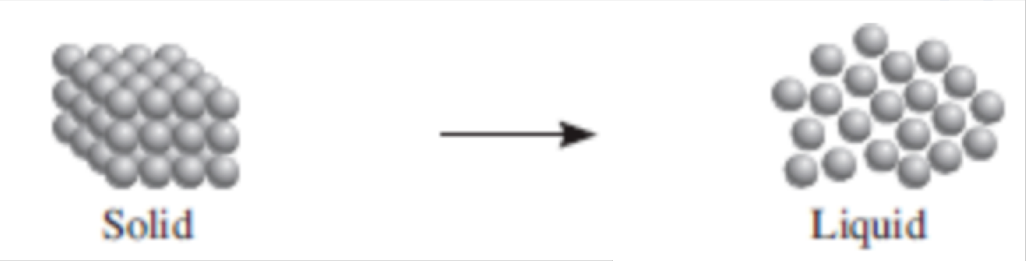
$$Al_2O_3 (s) + 3H_2(g) \rightarrow 2\ Al(s) + 3H_2O(g)$$

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

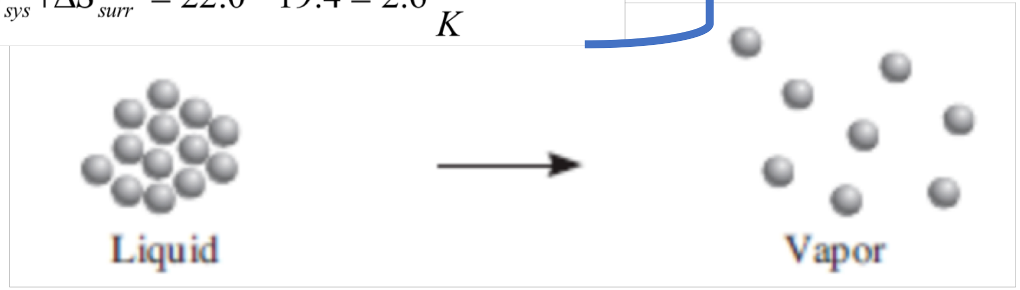


$$\Delta S_{sys} = \frac{q_{rev}}{T} = \frac{(1mol)(6.01x10^3\, J/mol)}{273K} = 22.0\frac{J}{K}$$

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

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

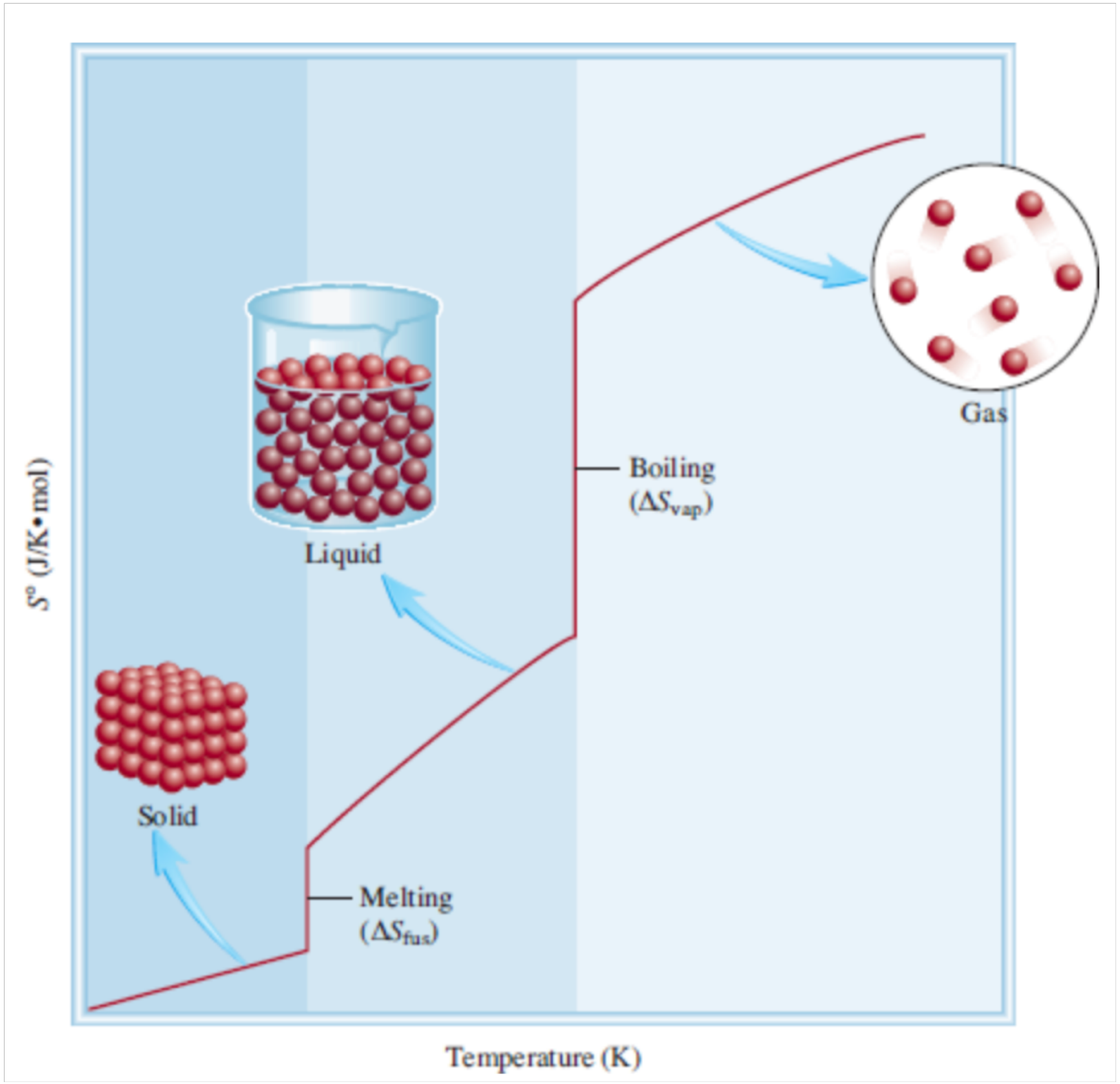
ΔS calculation for melting ice in the palm of your hand



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°_{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, ΔG°

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)

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

Gibbs Free Energy & Spontaneity

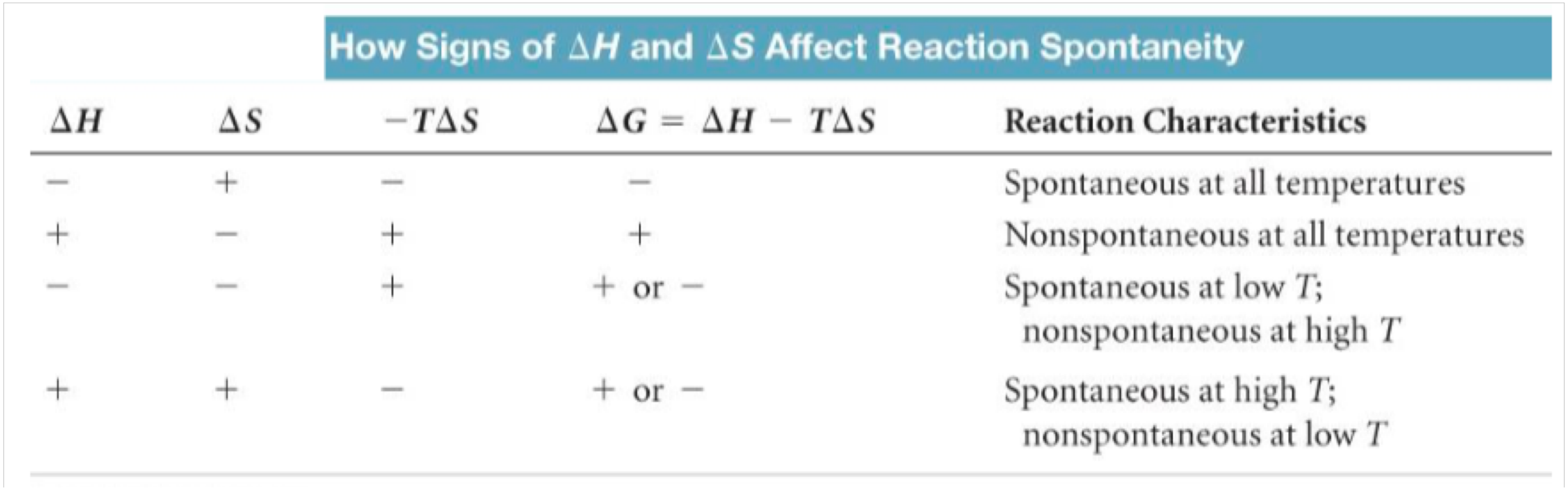
$\Delta G < 0$ (negative), the process is spontaneous

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

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

ΔH	**ΔS**	**ΔG**	**Spontaneous?**
negative	positive		
positive	negative		
negative	negative		
positive	positive		

Gibbs Free Energy & Spontaneity



How Signs of ΔH and ΔS Affect Reaction Spontaneity

ΔH	ΔS	$-T\Delta S$	$\Delta G = \Delta H - T\Delta S$	**Reaction Characteristics**
−	+	−	−	Spontaneous at all temperatures
+	−	+	+	Nonspontaneous at all temperatures
−	−	+	+ or −	Spontaneous at low T; nonspontaneous at high T
+	+	−	+ or −	Spontaneous at high T; 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 ΔG° 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

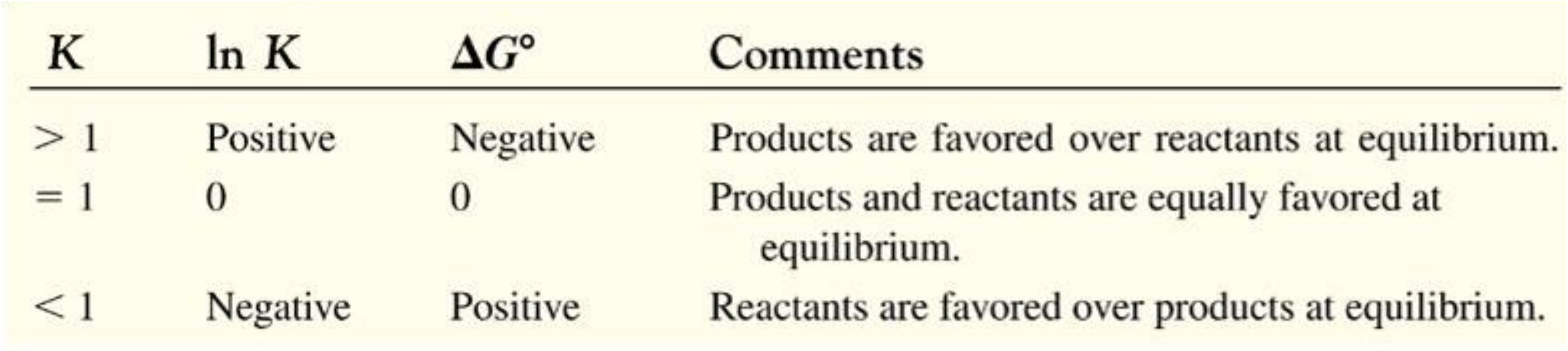
(Under standard conditions, all concentrations are 1M, so $Q = 1$, $\ln Q = 0$, and $\Delta G = \Delta G^\circ$)

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.

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

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

$\Delta G° = 0$ the reaction is at equilibrium

The magnitude of $\Delta G°$ indicates how far the standard state is from equilibrium
(more negative $\Delta G°$ = 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 1.6×10^{-14}

A: 79kJ/mol

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

2. For the following reaction:

$$2NO_2(g) \longrightarrow N_2O_{4(g)}$$

(a) Using data from Appendix 2, calculate ΔG° at 298K

(b) Calculate ΔG 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 1.6×10^{-5} at 25˚C

From Table:

ΔH˚$_f$ (kJ/mol)	**S˚ (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