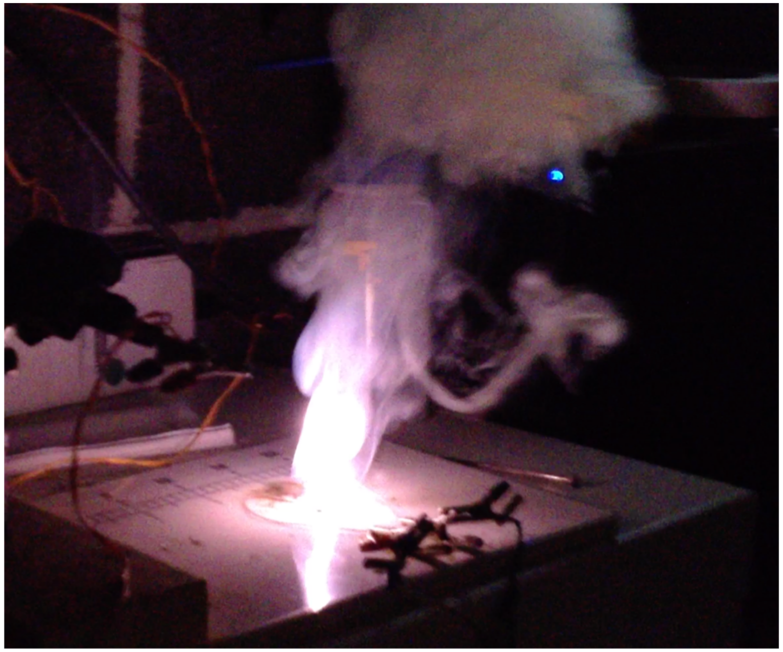
Chapter 15

Entropy and Gibbs Energy



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

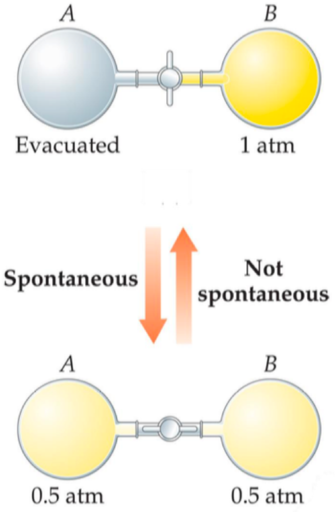
Free Energy (G):

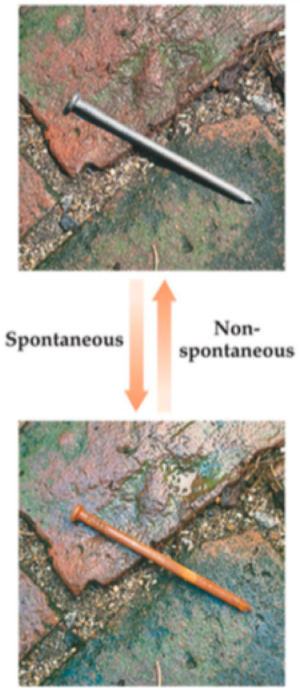
- Used to predict whether a process will occur spontaneously
- Spontaneously = without assistance
- Spontaneous process = one that will occur under a given set of conditions
- Depends on enthalpy, entropy, and temperature

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

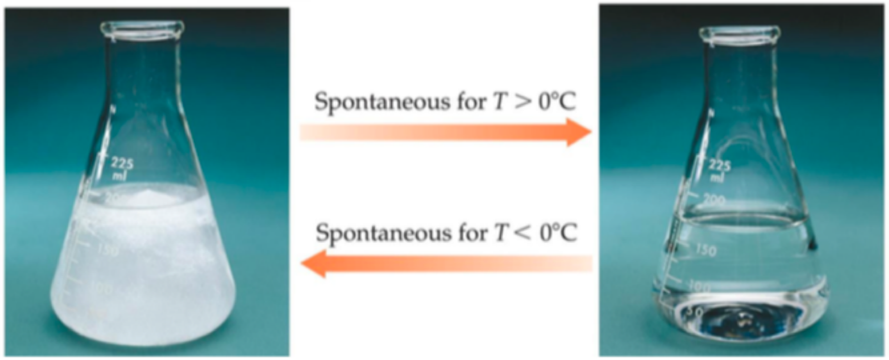
Spontaneous Processes

- 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



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)

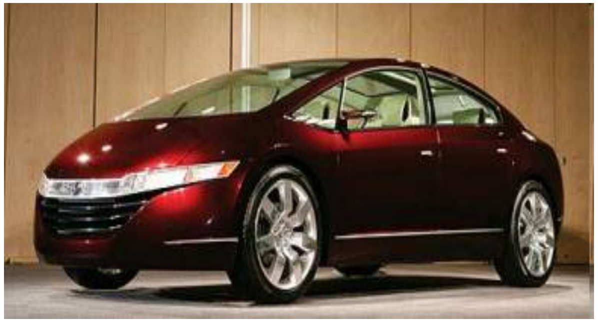
(d) Sublimation of CO_2(s) at -100˚C, 1 atm (CO_2 sublimation point is -78˚C, 1 atm)

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

Enthalpy & Spontaneity

Reaction of H_2 & O_2 to from H_2O

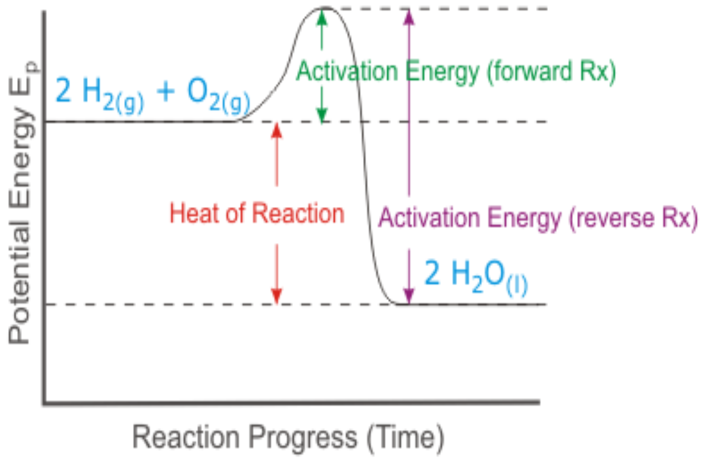
- Used in fuel cells
- Exothermic reaction
- ΔH = -286 kJ/mol
- Favors H_2O production



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

Reality at room temp:

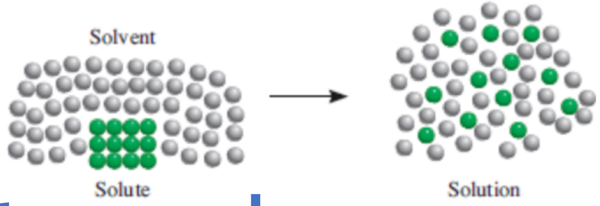
- Not a spontaneous reaction
- H_2 & O_2 remain unreacted
- No water is formed without added energy to initiate
- E_{act} = +112kJ/mol – too high



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

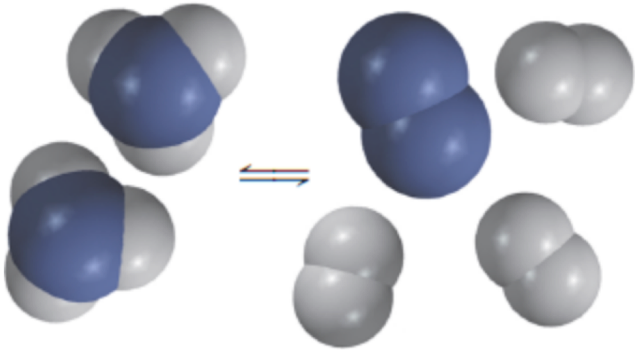
Also need to consider entropy

Entropy (S)



Entropy is defined as a measure of the randomness or disorder of a system, or how spread out a system's energy is

- 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)



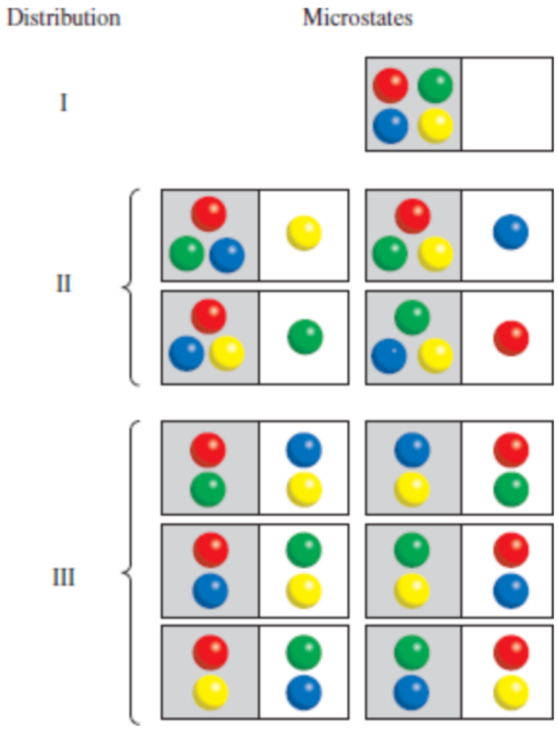
Entropy & Microstates

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.

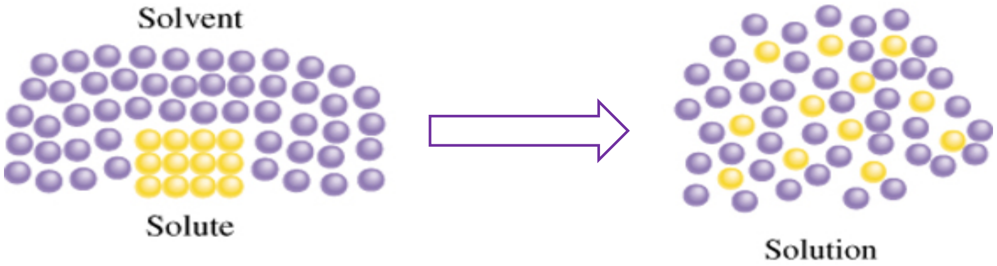


$$\Delta S = S_f - S_i$$
$$= k \ln W_f - k \ln W_i$$
$$= k \ln (W_f/W_i)$$

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

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 or those with large charges) this results in an overall decrease in entropy.

Dissolution Equation	$\Delta S^{\circ}_{\text{soln}}$ (J/k · mol)
$NH_4NO_3\ (s) \rightarrow NH_4^+\ (aq) + NO_3^-\ (aq)$	108.1
$AlCl_3\ (s) \rightarrow Al^{3+}\ (aq) + 3Cl^-\ (aq)$	−253.2
$FeCl_3\ (s) \rightarrow Fe^{3+}\ (aq) + 3Cl^-\ (aq)$	−266.1

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

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

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

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

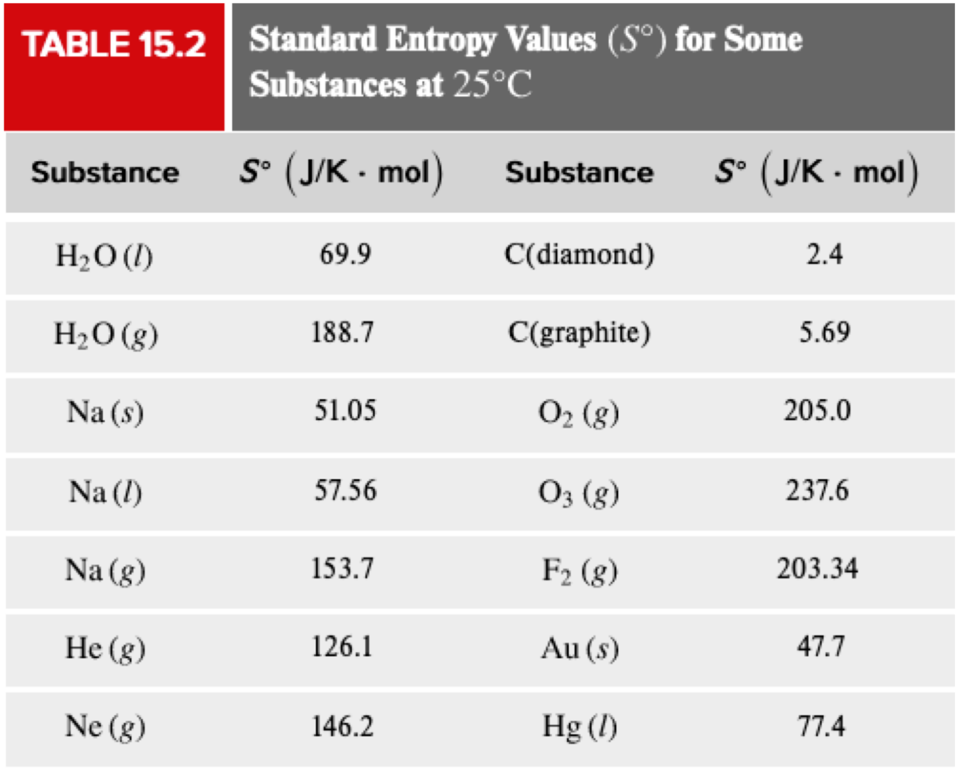
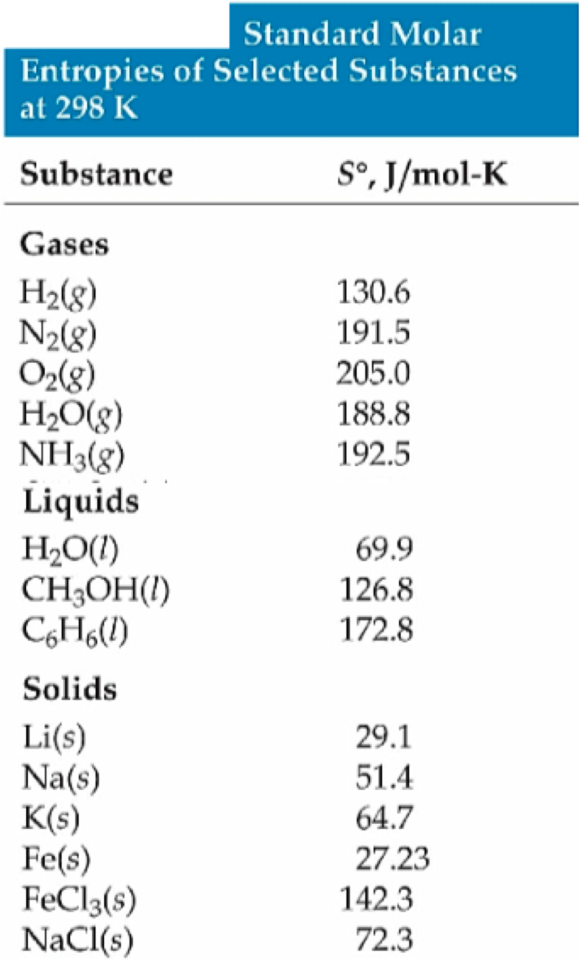


TABLE 15.2 Standard Entropy Values (S°) for Some Substances at 25°C

Substance	S° (J/K · mol)	Substance	S° (J/K · mol)
$H_2O\,(l)$	69.9	C(diamond)	2.4
$H_2O\,(g)$	188.7	C(graphite)	5.69
$Na\,(s)$	51.05	$O_2\,(g)$	205.0
$Na\,(l)$	57.56	$O_3\,(g)$	237.6
$Na\,(g)$	153.7	$F_2\,(g)$	203.34
$He\,(g)$	126.1	$Au\,(s)$	47.7
$Ne\,(g)$	146.2	$Hg\,(l)$	77.4



Standard Molar Entropies of Selected Substances at 298 K

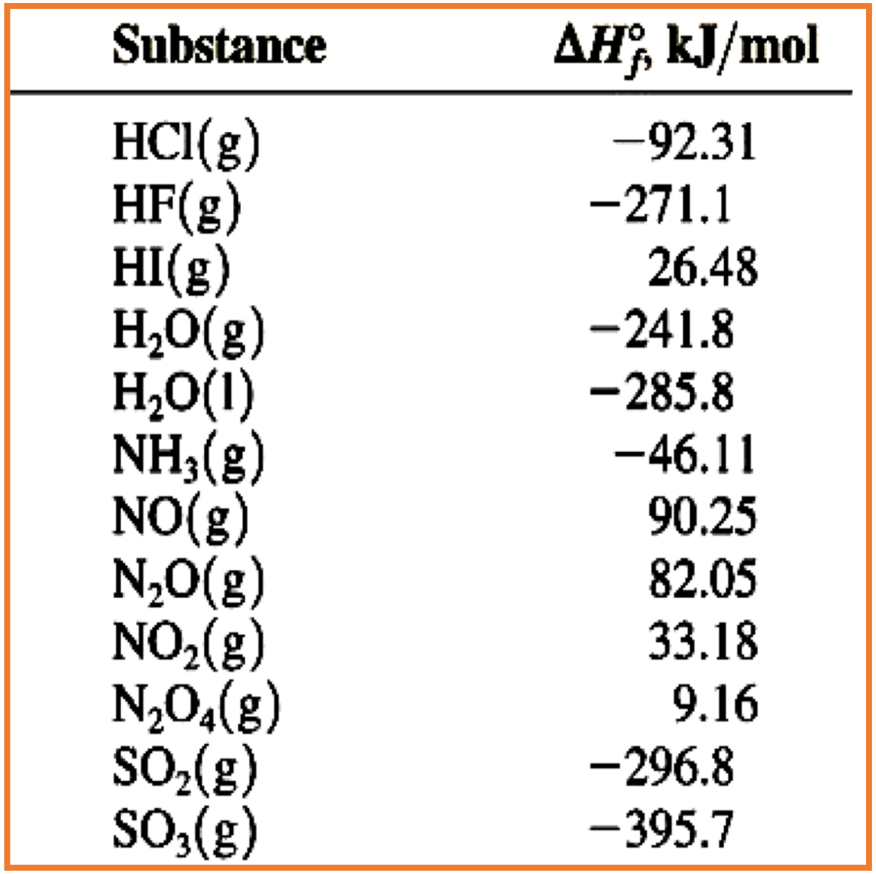
Substance	S°, J/mol-K
Gases	
$H_2(g)$	130.6
$N_2(g)$	191.5
$O_2(g)$	205.0
$H_2O(g)$	188.8
$NH_3(g)$	192.5
Liquids	
$H_2O(l)$	69.9
$CH_3OH(l)$	126.8
$C_6H_6(l)$	172.8
Solids	
$Li(s)$	29.1
$Na(s)$	51.4
$K(s)$	64.7
$Fe(s)$	27.23
$FeCl_3(s)$	142.3
$NaCl(s)$	72.3

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

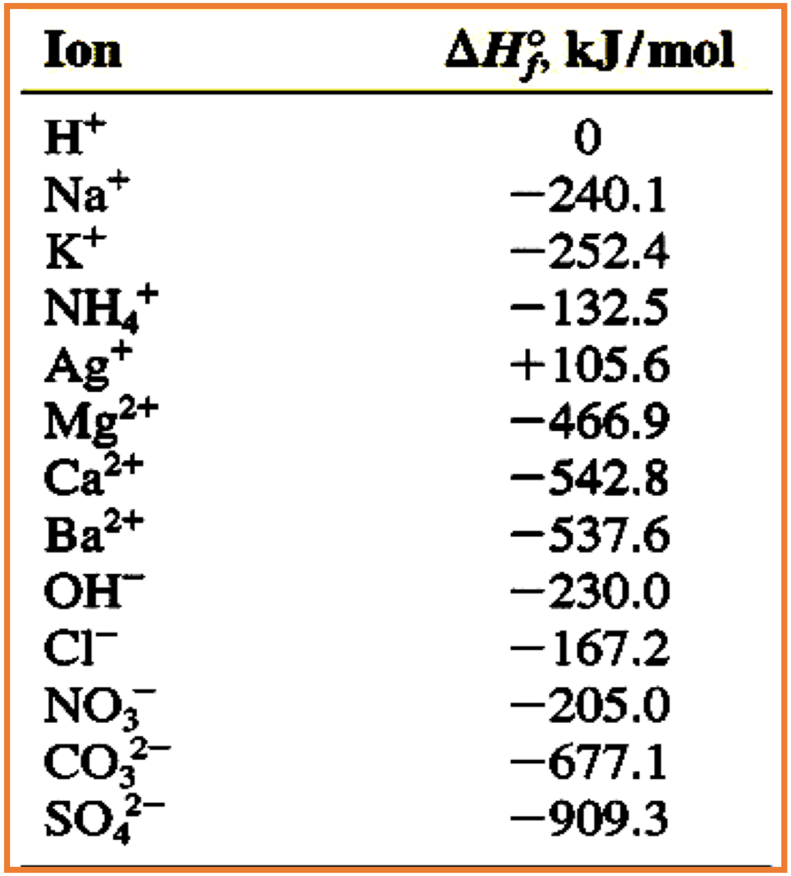
For similar molecules, S° tends to increase with:

- Increasing molar mass
- Increased number of atoms in formula

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
Enthalpy values will be needed for Gibbs Energy Calcs.

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

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

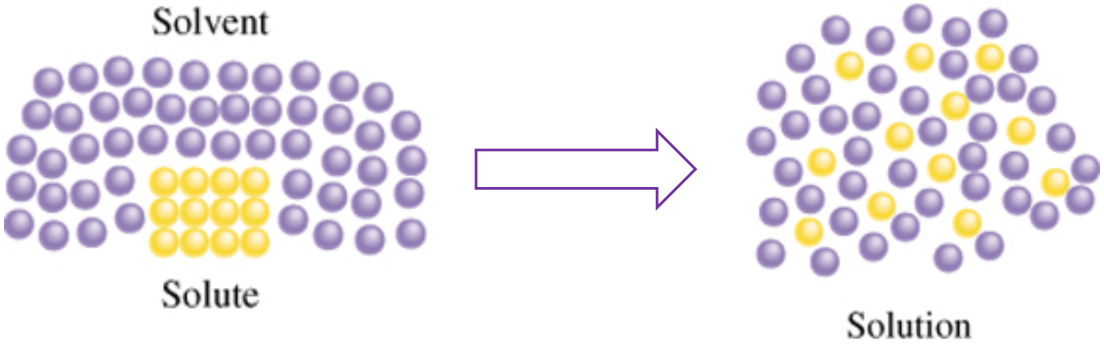
Three Laws of Thermodynamics

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:

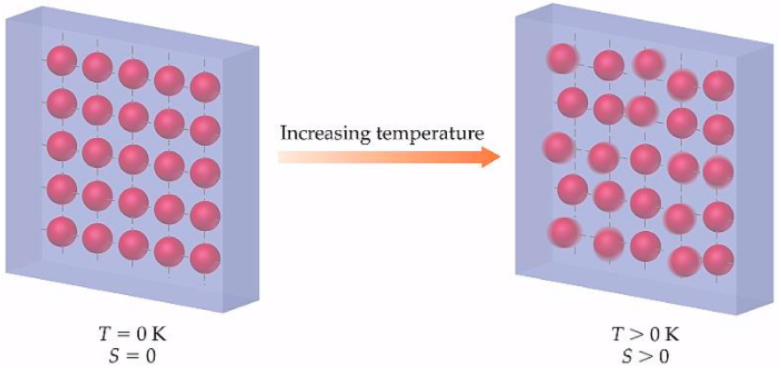
- The entropy of the Universe ($\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$) increases for spontaneous processes
- For spontaneous (irreversible) processes: $\Delta S_{univ} > 0$
- For reversible processes: $\Delta S_{univ} = 0$



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.

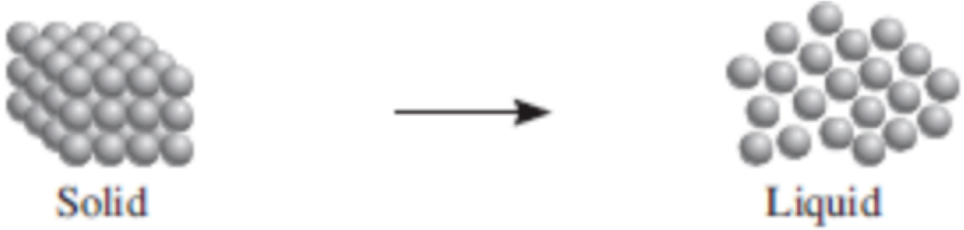


Calculating Entropy (S) from ΔH

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

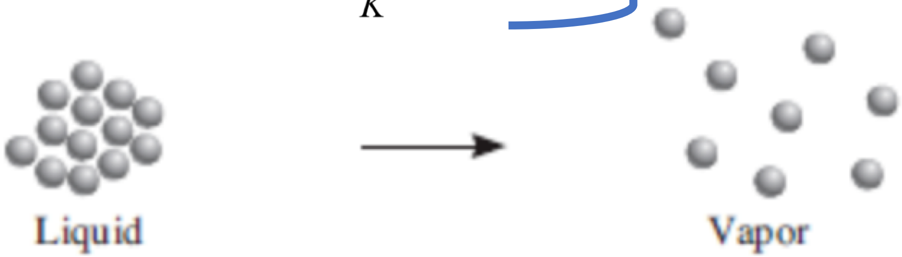


$$\Delta S_{sys} = \frac{q_{rev}}{T} = \frac{(1mol)(6.01x10^3\,J/mol)}{273K} = 22.0\frac{J}{K}$$

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

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

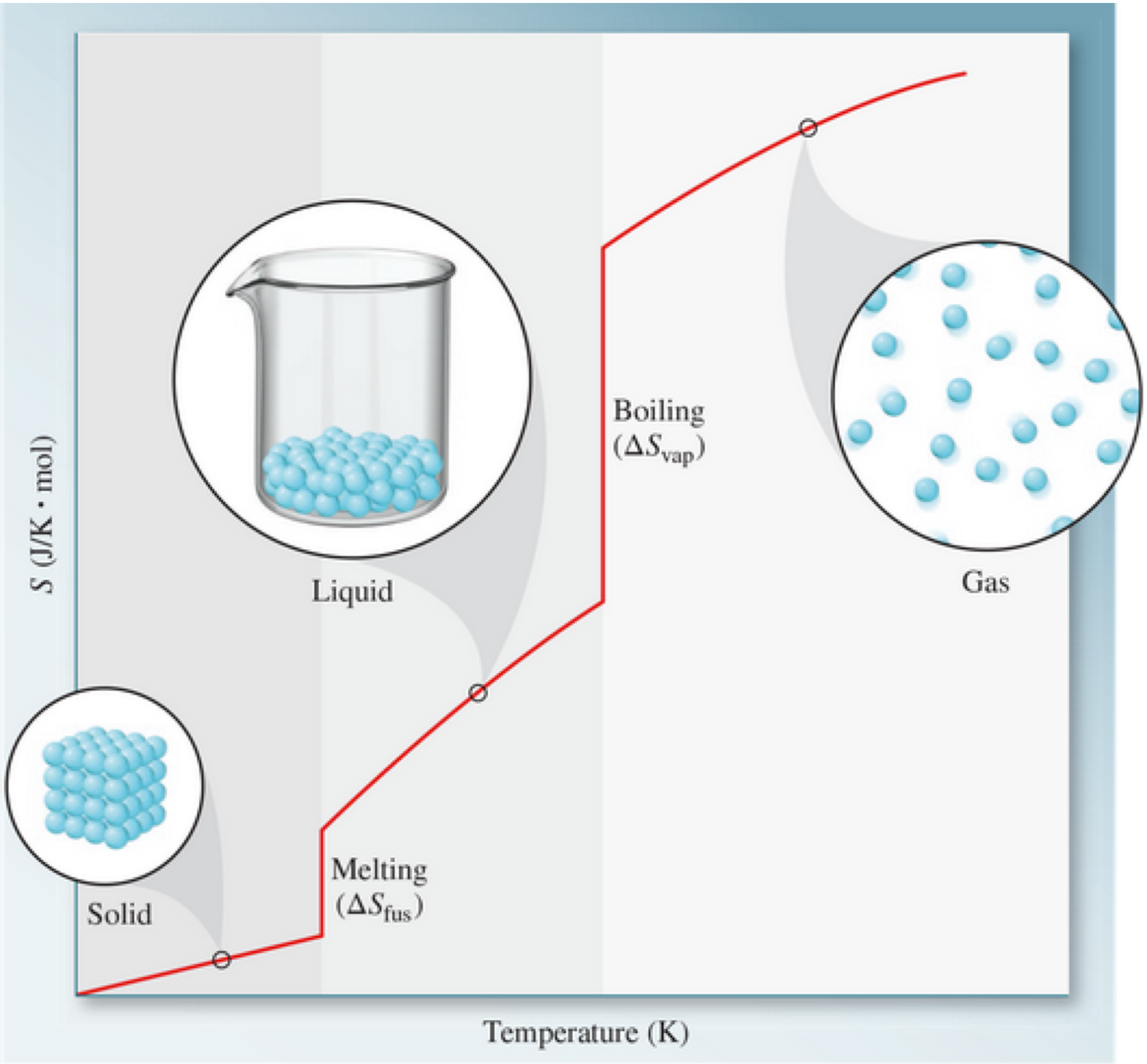
ΔS calculation for melting ice in the palm of your hand



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	negative	yes
positive	negative	positive	no
negative	negative	?	Temp Dependent
positive	positive	?	Temp Dependent

Gibbs Free Energy & Spontaneity

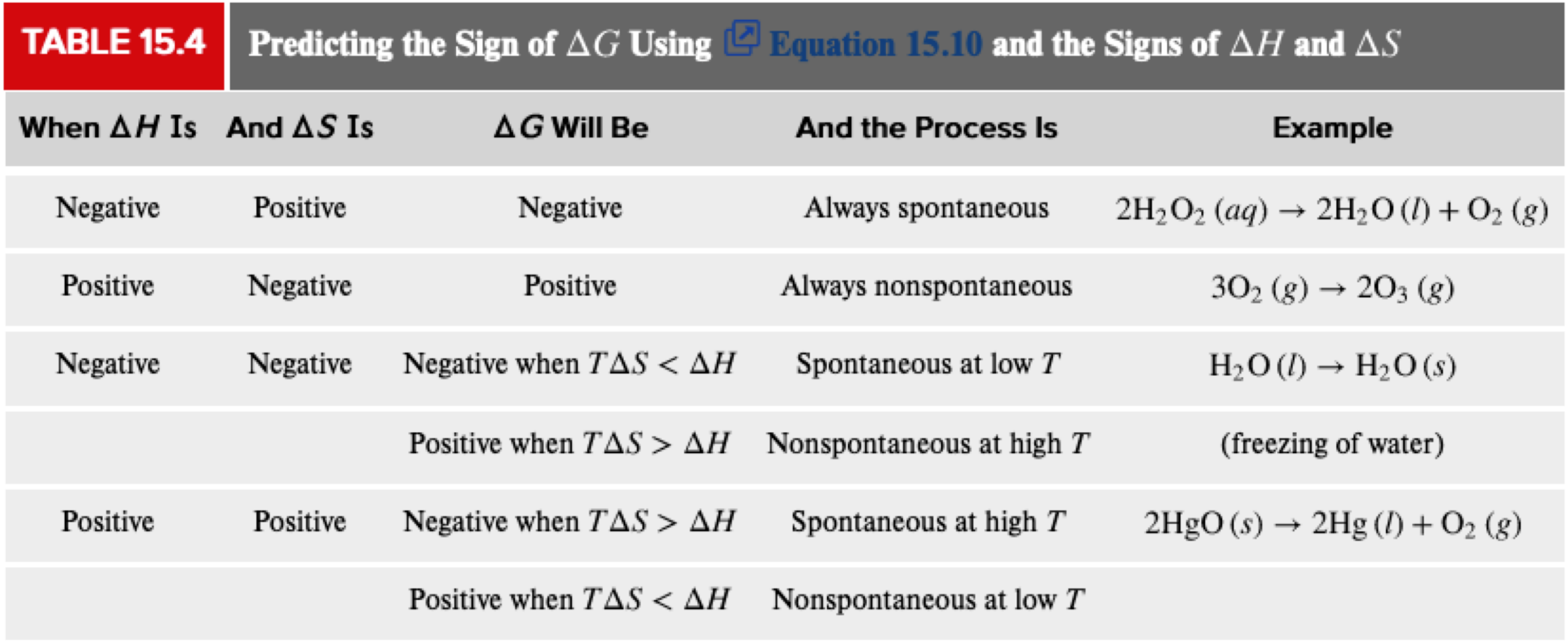


TABLE 15.4 Predicting the Sign of ΔG Using Equation 15.10 and the Signs of ΔH and ΔS

When ΔH Is	And ΔS Is	ΔG Will Be	And the Process Is	Example
Negative	Positive	Negative	Always spontaneous	$2H_2O_2\,(aq) \rightarrow 2H_2O\,(l) + O_2\,(g)$
Positive	Negative	Positive	Always nonspontaneous	$3O_2\,(g) \rightarrow 2O_3\,(g)$
Negative	Negative	Negative when $T\Delta S < \Delta H$	Spontaneous at low T	$H_2O\,(l) \rightarrow H_2O\,(s)$
		Positive when $T\Delta S > \Delta H$	Nonspontaneous at high T	(freezing of water)
Positive	Positive	Negative when $T\Delta S > \Delta H$	Spontaneous at high T	$2HgO\,(s) \rightarrow 2Hg\,(l) + O_2\,(g)$
		Positive when $T\Delta S < \Delta H$	Nonspontaneous at low T	

Gibbs Free Energy & Spontaneity

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

(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