4. The Second Law of Thermodynamics

CHM 301

Cal Poly Pomona

Dr. Yujung Dong

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Spontaneous Processes

At 20°C and 1 atm, ice melts

At -10°C and 1 atm, water freezes

Sugar dissolves into water

A ball rolling downhills

An ice pack cools down our muscles

Combustion (reaction with O_2) reaction of fuel:

fuel + O_2 → CO_2 + H_2O

A spontaneous process is a **naturally occurring process** that once started will continue to **happen without outside intervention**.
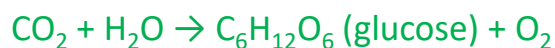
Nonspontaneous Processes

At 20°C and 1 atm, water freezes

Precipitation of dissolved sugar particles

A ball rolling uphills

Compression of gases

Photosynthesis (only proceeds with light):

$CO_2 + H_2O \rightarrow C_6H_{12}O_6$ (glucose) + O_2

A nonspontaneous process is an **unnatural** process that after it is started **will NOT continue to happen without outside intervention**.

# How do you determine if a process is spontaneous?

"Exothermic" does NOT always mean spontaneous.

Cold Pack

- When the membrane is ruptured, the solid mixes with and dissolves in water.
- Endothermic reaction (surroundings are cooled down)
- **Endothermic, but spontaneous.**

- NH_4^+ and NO_3^- ions in solution are 1) more spread out and 2) have more freedom of motion.

Spontaneous does NOT mean fast:
  Rusting of iron is a slow but happens without intervention.

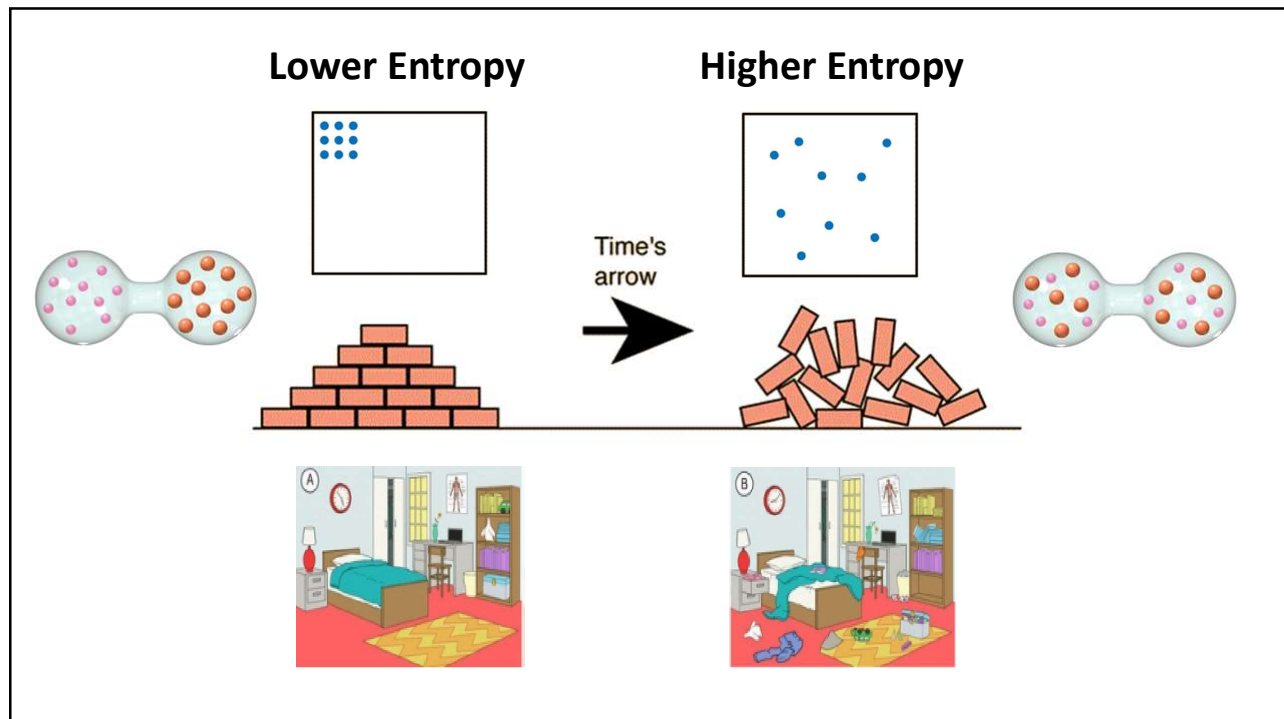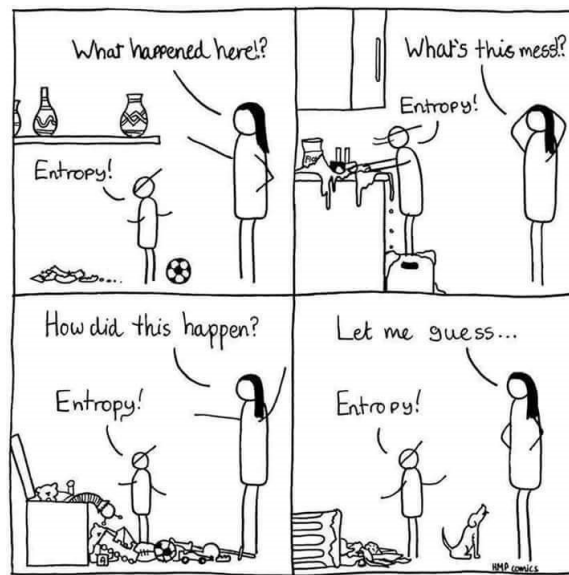Ions in
crystalline solid

Hydrated ions
in solution

$NH_4NO_3(s)$ $NH_4^+(aq) + NO_3^-(aq)$
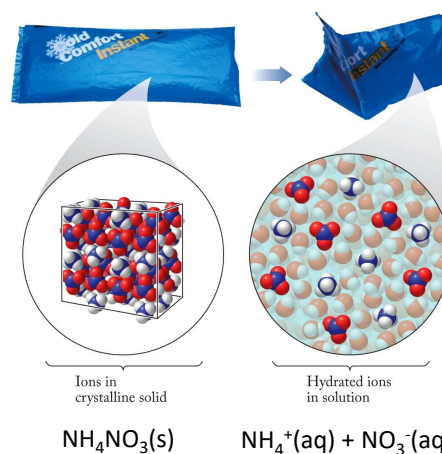
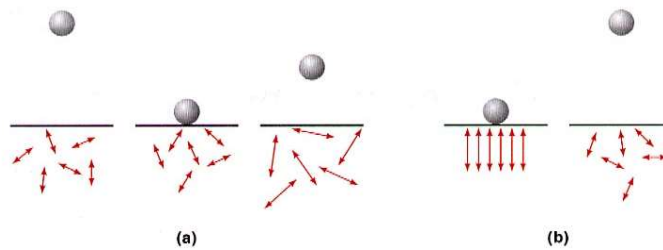# Entropy (S)

• a measure of how *dispersed* the system is

Second Law of Thermodynamics

• The **entropy of the universe increases** in any *spontaneous* process ($\Delta S_{univ} > 0$).

• Easy way to think of it: degree of chaos, disorder
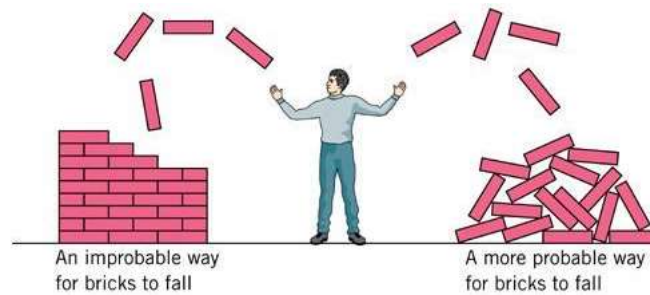

Lower Entropy   **Higher Entropy**

Time's arrow

Statistical View of Entropy/2nd Law

There is a higher **probability** to have a more dispersed arrangement.

(There are more ways to be messy than to be tidy.)

An improbable way for bricks to fall

A more probable way for bricks to fall

Ways to have lower dispersion   **Ways to have higher dispersion**

2   4
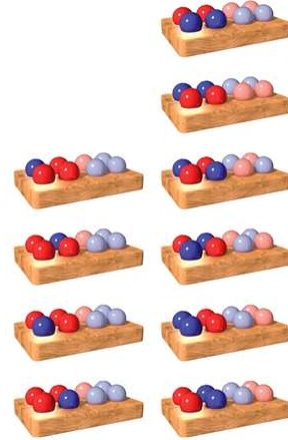
Ways to have lower dispersion   **Ways to have higher dispersion**

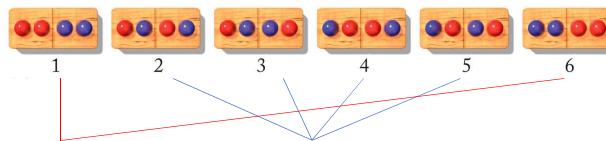2   68

Entropy and Number of Probable Arrangements(W)

- Boltzmann related:
  - *Entropy* and **number of probable arrangements** (W)

    S = k$_B$ ln W

- Boltzmann constant $k_{\mathrm{B}} = \dfrac{R}{N_{\mathrm{A}}} = \dfrac{8.314\,\frac{\mathrm{J}}{\mathrm{mol}\cdot\mathrm{K}}}{6.0221\times10^{23}/\mathrm{mol}} = 1.381\times10^{-23}\ \mathrm{J/K}$
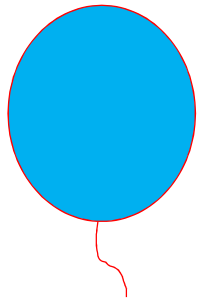
    same macrostate   same macrostate
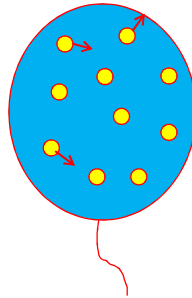   each are different microstates => six microstates
    number of probable arrangements (W) = 6

Ref: Macrostate vs. Microstate

W incorporates particle movement (momentum) as well as position: translational, rotational, vibrational
- quantized

| Macrostate:
P, V, T | Microstate 1:
particle #1: (x, y, z), v
particle #2: (x, y, z), v
particle #3: (x, y, z), v
… | Microstate 2:
particle #1: (x, y, z), v
particle #2: (x, y, z), v
particle #3: (x, y, z), v
… | … |

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Factors that Affect Entropy

- **Mixing**: higher mixing => higher entropy
- (higher probability to be mixed)

n_A, V_A n_B, V_B $n = n_A + n_B$ $V = V_A + V_B$

P, T P, T P, T
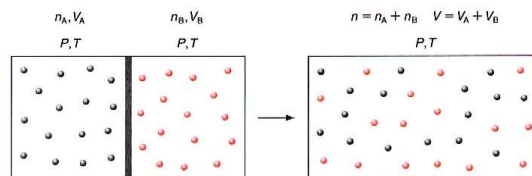
- **Volume**: larger volume => higher entropy
- (higher probability to occupy higher volume)

Volume = V_1 Volume = V_2
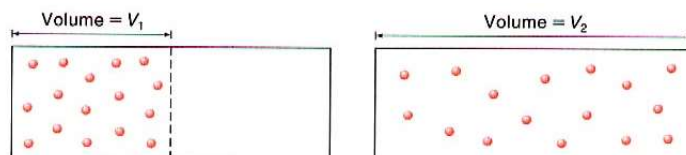
Factors that Affect Entropy

- **Temperature**: higher temperature => higher entropy
- (higher kinetic energy with more motion)

- **Number of Particles**: more molecules => higher entropy
- (more ways to arrange)
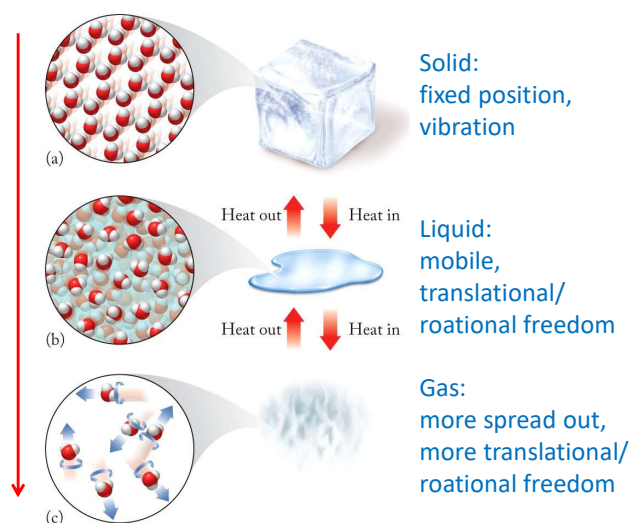
Factors that Affect Entropy

- **Physical State**:

    solid < liquid < gas

    => higher entropy

(higher degree of freedom to move around)

more spread out/
more freedom of
movement

Solid:
fixed position,
vibration

Heat out   Heat in

Liquid:
mobile,
translational/
roational freedom

Heat out   Heat in

Gas:
more spread out,
more translational/
roational freedom

Third Law of Thermodynamics

a perfect *crystalline solid* has
zero entropy at absolute zero (0 K).
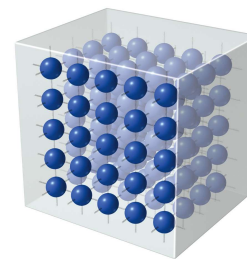
S=0 at T = 0 K

- If the particles of a crystalline solid are perfectly aligned and in their lowest possible energy states, the crystal has only one microstate, therefore, entropy is zero.
$$S = k_B \ln W = k_B \ln 1 = 0$$
- Provides a point of reference or baseline for entropy.

- **We can calculate *absolute* entropy values (S)** unlike enthalpy values, for which we could only calculate the **Δ**H values

Standard Molar Entropy

Third law of thermodynamics

⇒reference point for zero entropy at 0 K

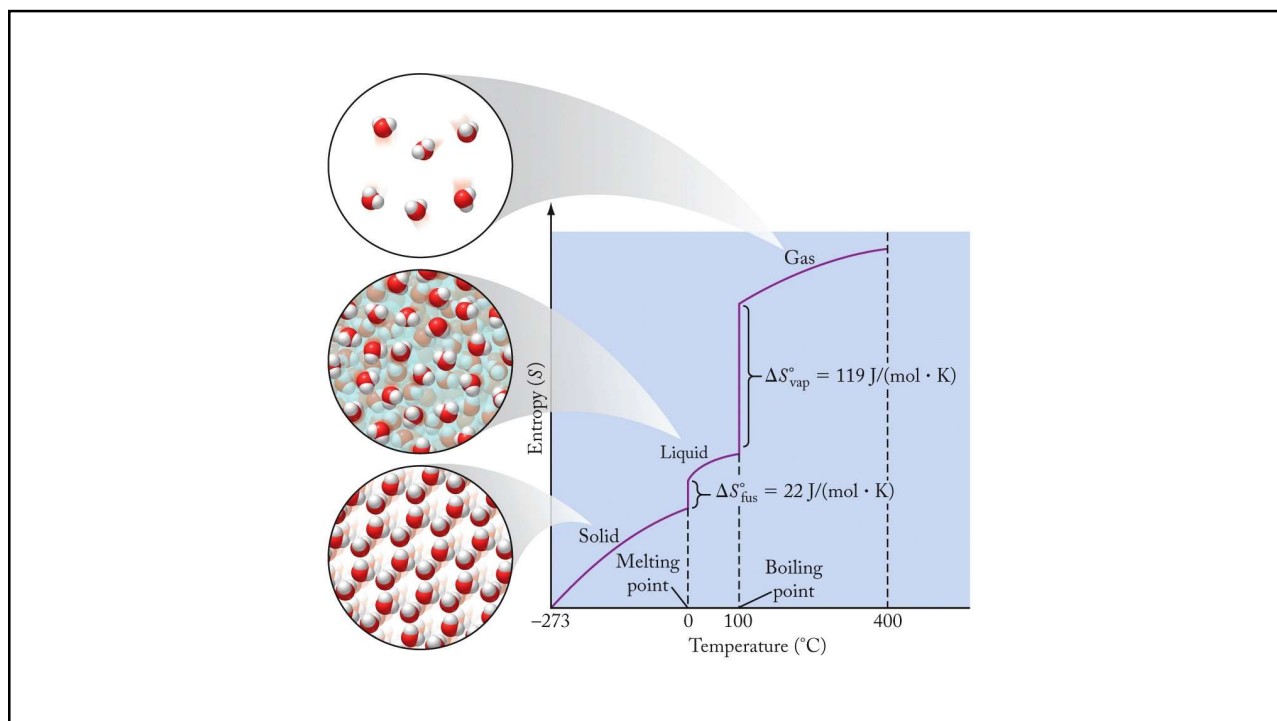⇒We know the absolute entropy values of substances.

Standard molar entropy (S°):

The absolute entropy of 1 mol of a substance in its standard state at 298 K and 1 bar (~1 atm) of pressure

- $S_{solid} < S_{liquid} < S_{gas}$

TABLE 18.1   Standard Entropies of Some Typical Substances at 298.15 K

Substance	$S°$ (J mol^{-1} K^{-1})	Substance	$S°$ (J mol^{-1} K^{-1})	Substance	$S°$ (J mol^{-1} K^{-1})
Ag(s)	42.55	CaO(s)	40	N$_2$(g)	191.5
AgCl(s)	96.2	Ca(OH)$_2$(s)	76.1	NH$_3$(g)	192.5
Al(s)	28.3	CaSO$_4$(s)	107	NH$_4$Cl(s)	94.6
Al$_2$O$_3$(s)	51.0	CaSO$_4 \cdot \frac{1}{2}$H$_2$O(s)	131	NO(g)	210.6
C(s) (graphite)	5.69	CaSO$_4$·2H$_2$O(s)	194.0	NO$_2$(g)	240.5
CO(g)	197.9	Cl$_2$(g)	223.0	N$_2$O(g)	220.0
CO$_2$(g)	213.6	Fe(s)	27	N$_2$O$_4$(g)	304
CH$_4$(g)	186.2	Fe$_2$O$_3$(s)	90.0	Na(s)	51.0
CH$_3$Cl(g)	234.2	H$_2$(g)	130.6	Na$_2$CO$_3$(s)	136
CH$_3$OH(l)	126.8	H$_2$O(g)	188.7	NaHCO$_3$(s)	102
CO(NH$_2$)$_2$(s)	104.6	H$_2$O(l)	69.96	NaCl(s)	72.38
CO(NH$_2$)$_2$(aq)	173.8	HCl(g)	186.7	NaOH(s)	64.18
C$_2$H$_2$(g)	200.8	HNO$_3$(l)	155.6	Na$_2$SO$_4$(s)	149.4
C$_2$H$_4$(g)	219.8	H$_2$SO$_4$(l)	157	O$_2$(g)	205.0
C$_2$H$_6$(g)	229.5	HC$_2$H$_3$O$_2$(l)	160	PbO(s)	67.8
C$_8$H$_{18}$(l)	466.9	Hg(l)	76.1	S(s)	31.9
C$_2$H$_5$OH(l)	161	Hg(g)	175	SO$_2$(g)	248.5
Ca(s)	41.4	K(s)	64.18	SO$_3$(g)	256.2
CaCO$_3$(s)	92.9	KCl(s)	82.59		
CaCl$_2$(s)	114	K$_2$SO$_4$(s)	176		

The Second Law of Thermodynamics

The entropy of the universe increases
in any *spontaneous* process.

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} > 0$$

- If $\Delta S_{univ} > 0$, the process is spontaneous.
- If $\Delta S_{univ} < 0$, the process is nonspontaneous.

Entropy and Heat

- When a ball bounces, in reality, all the gravitational potential is not converted into kinetic energy.
- Part of it is converted into heating the ground. Therefore, due to the loss of energy, the ball does not bounce back up to its original position.
- Same thing with heat engines, energy lost into heat cannot be easily collected and used.
- It can be seen that heat is a lower grade of energy, or loss of energy because the degree of freedom of the energy is high.
- The relation of heat and entropy can be seen in these examples: heat as energy form can be seen as increase in randomness.
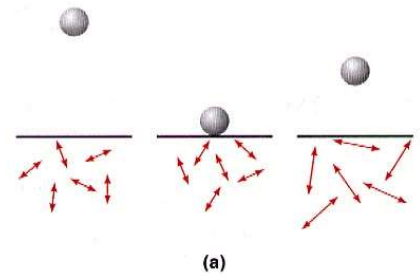
(a)

Figure 5.2

Entropy and Heat

- Entropy (S) increases with heat (q) : ΔS is proportional to q
- Heating particles that are already hot produces smaller gain in entropy than heating the same particles at a lower temperature.
  - ΔS is inversely proportional to T

$$\Delta S = \frac{q}{T}$$

$$\Delta S_{sys} = \frac{q_{sys}}{T} \qquad \Delta S_{sur} = \frac{q_{surr}}{T}$$

- For infinitesimal changes,

$$dS = \frac{dq_{rev}}{T}$$

Entropy and Heat

$$dS = \frac{dq_{rev}}{T}$$

➤ integrate

$$\Delta S = \int_{T_1}^{T_2} \frac{dq_{rev}}{T}$$

➤ from chapter 3, $dq_{rev} = C_p dT$

$$\Delta S = \int_{T_1}^{T_2} \frac{C_p}{T} dT$$

➤ at T=0, S=0 (Third Law)

➤ set T_1=0,

$$S_{T_2} - S_0 = \int_0^{T_2} \frac{C_p}{T} dT$$

$$S_{T_2} = \int_0^{T_2} \frac{C_p}{T} dT$$

➤ absolute entropy value at T_2

Second Law (ΔS_{univ} >0) in Other Words

$$dS_{univ} = dS_{sys} + dS_{surr} > 0$$

: second law of thermodynamics

$$dS_{surr} = \frac{dq_{surr}}{T}$$

$$= dS_{sys} + \frac{dq_{surr}}{T} > 0$$

$$q_{surr} = -q_{sys}$$

same thing

$$= dS_{sys} - \frac{dq_{sys}}{T} > 0$$

at const P, $\Delta H = q$

$$= dS_{sys} - \frac{dH_{sys}}{T} > 0$$

multiply each side with (-T)

$$dH_{sys} - T d\Delta S_{sys} < 0$$

Second Law (ΔS_{univ} >0) in Other Words

The second law of thermodynamics:

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} > 0$$

The entropy of the universe increases in any spontaneous processes

translates to:

$$\Delta H_{sys} - T\Delta S_{sys} < 0 \;\; or \;\; \Delta G_{sys} < 0 \text{ (or just } \Delta G<0)$$

The Gibbs free energy of the system decreases in any spontaneous processes

Therefore,   **ΔG = Δ H − T Δ S < 0**

for any spontaneous processes

Only another form of second law!

Gibbs Free Energy and Spontaneity

- When   **ΔG = Δ H − T Δ S < 0**   **Spontaneous**   Exergonic
- When   **ΔG = Δ H − T Δ S = 0**   **Equilibrium**
- When   **ΔG = Δ H − T Δ S > 0**   **Nonspontaneous**   Endergonic

ΔG = Δ H − T Δ S

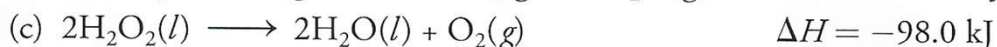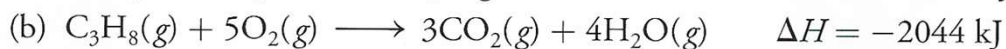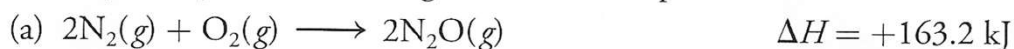- Two factors that contribute to **ΔG < 0** (spontaneous)
    1) Increase in entropy **ΔS > 0**
    2) Exothermic **ΔH < 0**

Signs of ΔG, Δ H, and Δ S

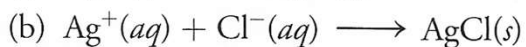$$\Delta G = \Delta H - T \Delta S < 0 : \text{Spontaneous}$$

ΔH	ΔS	ΔG	Spontaneity
−	+	Always < 0	Always spontaneous
−	−	< 0 at lower temperature	Spontaneous at lower temperature
+	+	< 0 at higher temperature	Spontaneous at higher temperature
+	−	Always > 0	Never spontaneous

Would you expect the following reactions to be spontaneous?

(a) $2N_2(g) + O_2(g) \longrightarrow 2N_2O(g)$ $\qquad\qquad \Delta H = +163.2 \text{ kJ}$

(b) $C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(g)$ $\qquad \Delta H = -2044 \text{ kJ}$

(c) $2H_2O_2(l) \longrightarrow 2H_2O(l) + O_2(g)$ $\qquad\qquad\qquad \Delta H = -98.0 \text{ kJ}$

(*Hint:* Remember how entropy and enthalpy affect spontaneity.)

What change in temperature would make the process spontaneous?

(a) $H_2O(l) \longrightarrow H_2O(g)$

(b) $Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$

At constant volume?

Second law of thermodynamics :

If $\Delta S_{univ} > 0$, the process is spontaneous.

- At constant P, equivalent to $\Delta G_{sys} < 0$ (G = H-TS)

- At constant V, equivalent to $\Delta A_{sys} < 0$ (A = U-TS: Helmholtz energy)

Review: Calculating ΔH_{rxn}^o

Since we do not know the absolute enthalpy values of substances, we use enthalpy of formation (ΔH_f^o) of the reactants and products to calculate the enthalpy of reactions at standard state.

ΔH_{rxn}^o = [sum of ΔH_f^o of all the products]
$-$ [sum of ΔH_f^o of all the reactants]

$\Delta H_{rxn}^\circ = \sum n_p \Delta H_f^o \text{ (products)} - \sum n_r \Delta H_f^o \text{ (reactants)}$

Calculating $\Delta S_{rxn}°$ of Reactions

We use absolute entropy (S°) of reactants and products to calculate the enthalpy of reactions ($\Delta S_{rxn}°$) at standard state.

$$\Delta S_{rxn}° = \text{[sum of S° of all the products]}$$
$$- \text{[sum of S° of all the reactants]}$$

$$\Delta S°_{rxn} = \sum n_p S°(\text{products}) - \sum n_r S°(\text{reactants})$$

Calculating $\Delta G_{rxn}°$ of Reactions (1st method)

• $\Delta G = \Delta H - T \Delta S$. Therefore,

$$\Delta G_{rxn}° = \Delta H_{rxn}° - T \Delta S_{rxn}°$$

- Calculate the $\Delta G_{rxn}°$ for the following reaction at 298 K:

$$CO(NH_2)_2(aq) + H_2O(l) \longrightarrow CO_2(g) + 2NH_3(g)$$

urea
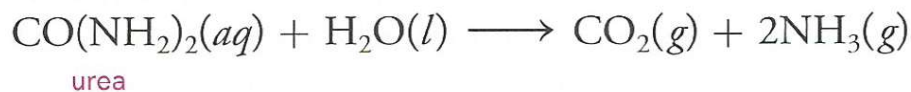
- Is the reaction exothermic or endothermic?

- Is the reaction spontaneous?

$\Delta H_{rxn}° = 1\ mol \times (-393.5)\ kJ\ mol^{-1} + 2\ mol \times (-46.19)\ kJ\ mol^{-1}$

$\qquad [1\ mol \times (-391.2\ )\ kJ\ mol^{-1} + 1\ mol \times (-285.9)\ kJ\ mol^{-1}]$

$= +191.2\ kJ > 0 \qquad$ endothermic

$\Delta S_{rxn}° = 1\ mol \times (213.6\ J\ mol^{-1} k^{-1} + 2\ mol \times 192.5\ J\ mol^{-1} k^{-1}$

$\qquad - [1\ mol\ 173.8\ J\ mol^{-1} K^{-1} + 1\ mol \times 69.96\ J\ mol^{-1} K^{-1}] = 354.8\ J\ K^{-1}$

$\Delta G_{rxn}° = \Delta H_{rxn}° - T\Delta S_{rxn}° = 191.2\ kJ - 298\ K \times 354.8\ J\ K^{-1} \times 10^{-3}\ kJ/J = 85.4\ kJ > 0$

Nonspontaneous

TABLE 6.2	Standard Enthalpies of Formation of Typical Substances		
Substance	$\Delta H_f°$ (kJ mol^{-1})	Substance	$\Delta H_f°$ (kJ mol^{-1})
Ag(s)	0	H$_2$O$_2$(l)	−187.6
AgBr(s)	−100.4	HBr(g)	−36
AgCl(s)	−127.0	HCl(g)	−92.30
Al(s)	0	HI(g)	26.6
Al$_2$O$_3$(s)	−1669.8	HNO$_3$(l)	−173.2
C(s) (graphite)	0	H$_2$SO$_4$(l)	−811.32
CO(g)	−110.5	HC$_2$H$_3$O$_2$(l)	−487.0
CO$_2$(g)	−393.5	Hg(l)	0
CH$_4$(g)	−74.848	Hg(g)	60.84
CH$_3$Cl(g)	−82.0	I$_2$(s)	0
CH$_3$I(g)	14.2	K(s)	0
CH$_3$OH(l)	−238.6	KCl(s)	−435.89
CO(NH$_2$)$_2$(s) (urea)	−333.19	K$_2$SO$_4$(s)	−1433.7
CO(NH$_2$)$_2$(aq)	−391.2	N$_2$(g)	0
C$_2$H$_2$(g)	226.75	NH$_3$(g)	−46.19
C$_2$H$_4$(g)	52.284	NH$_4$Cl(s)	315.4
C$_2$H$_6$(g)	−84.667	NO(g)	90.37
C$_2$H$_5$OH(l)	−277.63	NO$_2$(g)	33.8
Ca(s)	0	N$_2$O(g)	81.57
CaBr$_2$(s)	−682.8	N$_2$O$_4$(g)	9.67
CaCO$_3$(s)	−1207	N$_2$O$_5$(g)	11
CaCl$_2$(s)	−795.0	Na(s)	0
CaO(s)	−635.5	NaHCO$_3$(s)	−947.7
Ca(OH)$_2$(s)	−986.59	Na$_2$CO$_3$(s)	−1131
CaSO$_4$(s)	−1432.7	NaCl(s)	−411.0
CaSO$_4 \cdot \frac{1}{2}$H$_2$O(s)	−1575.2	NaOH(s)	−426.8
CaSO$_4 \cdot 2$H$_2$O(s)	−2021.1	Na$_2$SO$_4$(s)	−1384.5
Cl$_2$(g)	0	O$_2$(g)	0
Fe(s)	0	Pb(s)	0
Fe$_2$O$_3$(s)	−822.2	PbO(s)	−219.2
H$_2$(g)	0	S(s)	0
H$_2$O(g)	−241.8	SO$_2$(g)	−296.9
H$_2$O(l)	−285.9	SO$_3$(g)	−395.2

TABLE 18.1	Standard Entropies of Some Typical Substances at 298.15 K				
Substance	$S°$ (J mol^{-1} K^{-1})	Substance	$S°$ (J mol^{-1} K^{-1})	Substance	$S°$ (J mol^{-1} K^{-1})
Ag(s)	42.55	CaO(s)	40	N$_2$(g)	191.5
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- Calculate the $\Delta G_{rxn}°$ for the following reaction at 298 K:

$$4\,Fe\,(s) + 3\,O_2\,(g) \longrightarrow 2\,Fe_2O_3\,(s)$$
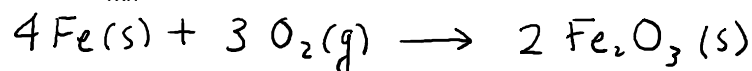
- Is the reaction exothermic or endothermic?
- Is the reaction spontaneous?

$\Delta H_{rxn}° = 2\,mol \times (-822.2)\,kJ\,mol^{-1} - \left[4\,mol \times 0\,kJ\,mol^{-1} + 3\,mol \times 0\,kJ\,mol^{-1}\right] = -1644.4\,kJ$

exothermic

$\Delta S_{rxn}° = 2\,mol \times 90.0\,J\,K^{-1}mol^{-1} - \left[4\,mol \times 27\,J\,K^{-1}mol^{-1} + 3\,mol \times 205.0\,J\,K^{-1}mol^{-1}\right]$

$= -543\,J\,K^{-1}$

$\Delta G_{rxn}° = \Delta H_{rxn}° - T\Delta S_{rxn}° = -1644.4\,kJ - 298\,K \times (-543)\,J\,K^{-1} \times 10^{-3}\,kJ/J$

$= -1483\,kJ < 0$ spontaneous

Calculating $\Delta G_{rxn}°$ of Reactions (2nd method)

- From standard free energy of formation ($\Delta G_f°$),

$$\Delta G_{rxn}° = [\text{sum of } \Delta G_f° \text{ of all the products}]$$
$$- [\text{sum of } \Delta G_f° \text{ of all the reactants}]$$

$$\Delta G°_{rxn} = \sum n_p \Delta G_f° \,(\text{products}) - \sum n_r \Delta G_f° \,(\text{reactants})$$

TABLE 18.2 Standard Free Energies of Formation of Typical Substances at 298.15 K

Substance	ΔG_f° (kJ mol^{-1})	Substance	ΔG_f° (kJ mol^{-1})	Substance	ΔG_f° (kJ mol^{-1})
Ag(s)	0	CaO(s)	−604.2	K$_2$SO$_4$(s)	−1316.4
AgCl(s)	−109.7	Ca(OH)$_2$(s)	−896.76	N$_2$(g)	0
Al(s)	0.00	CaSO$_4$(s)	−1320.3	NH$_3$(g)	−16.7
Al$_2$O$_3$(s)	−1576.4	CaSO$_4$·$\frac{1}{2}$H$_2$O(s)	−1435.2	NH$_4$Cl(s)	−203.9
C(s) (graphite)	0	CaSO$_4$·2H$_2$O(s)	−1795.7	NO(g)	+86.69
CO(g)	−137.3	Cl$_2$(g)	0	NO$_2$(g)	+51.84
CO$_2$(g)	−394.4	Fe(s)	0	N$_2$O(g)	+103.6
CH$_4$(g)	−50.79	Fe$_2$O$_3$(s)	−741.0	N$_2$O$_4$(g)	+98.28
CH$_3$Cl(g)	−58.6	H$_2$(g)	0	Na(s)	0
CH$_3$OH(l)	−166.2	H$_2$O(g)	−228.6	Na$_2$CO$_3$(s)	−1048
CO(NH$_2$)$_2$(s)	−197.2	H$_2$O(l)	−237.2	NaHCO$_3$(s)	−851.9
CO(NH$_2$)$_2$(aq)	−203.8	HCl(g)	−95.27	NaCl(s)	−384.0
C$_2$H$_2$(g)	+209	HNO$_3$(l)	−79.91	NaOH(s)	−382
C$_2$H$_4$(g)	+68.12	H$_2$SO$_4$(l)	−689.9	Na$_2$SO$_4$(s)	−1266.8
C$_2$H$_6$(g)	−32.9	HC$_2$H$_3$O$_2$(l)	−392.5	O$_2$(g)	0
C$_2$H$_5$OH(l)	−174.8	Hg(l)	0	PbO(s)	−189.3
C$_8$H$_{18}$(l)	+17.3	Hg(g)	+31.8	S(s)	0
Ca(s)	0	K(s)	0	SO$_2$(g)	−300.4
CaCO$_3$(s)	−1128.8	KCl(s)	−408.3	SO$_3$(g)	−370.4
CaCl$_2$(s)	−750.2				

• Calculate the ΔG_{rxn}° for the following reaction at 298 K using the second method :

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

$\Delta G_{rxn}^\circ = 2\,mol \times (-394.4)\ kJ\,mol^{-1} + 3\,mol \times (-228.6)\ kJ\,mol^{-1}$
$\qquad - \left[1\,mol \times (-174.8)\ kJ\,mol^{-1} + 3\,mol \times 0\ kJ\,mol^{-1} \right]$
$= -1299.8\ kJ < 0 \quad spontaneous$

Physical Meaning of Free Energy

- $\Delta E = q + w$: Energy is converted into work or heat.

- In systems such as combustion engines, we want to maximize the efficiency of energy: we want the energy to be converted into work rather than heat.

$$\Delta G = \Delta H - T\,\Delta S \Rightarrow \qquad \Delta H = \Delta G + T\,\Delta S$$

Gibbs Free Energy: maximum energy that can be theoretically be converted into useful work

not usable, portion of energy that spreads out

Physical Meaning of Free Energy

- Conversion of chemical energy into mechanical energy (ΔG) is never 100 % efficient due to T ΔS.

- Maximum efficiency when reversible.

- Some portion of ΔG (maximum energy) also wasted (non-reversible processes).

- Gasoline engine: 30% efficiency.

- **Reversible process**: happens so slowly that after an incremental change in the system has occurred, the process can be reversed by a tiny change that restores the original state of the system with no net flow of energy.

- In reality, a process can be only approximately reversible.

- When   **$\Delta G = \Delta H - T \Delta S < 0$**   **Spontaneous**
- When   **$\Delta G = \Delta H - T \Delta S = 0$**   **Equilibrium**
- When   **$\Delta G = \Delta H - T \Delta S > 0$**   **Nonspontaneous**

Spontaneity of Phase Changes

- H_2O (s) → H_2O(l) $\Delta H° = 6.01 \times 10^3$ J/mol; $\Delta S° = 22.0$ J/(mol · K)
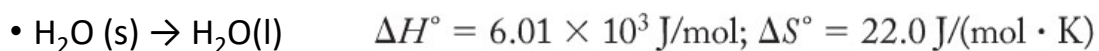
- $\Delta G = \Delta H - T\Delta S$

- We will assume that ΔH and ΔS does not change significantly with temperature.

➢ ($\Delta H = \Delta H°$, $\Delta S = \Delta S°$)

- $\Delta G = \Delta H° - T\Delta S°$ $\Delta G = (6.01 \times 10^3$ J/mol) $- T[22.0$ J/(mol · K)] $= 0$

$$T = \frac{6.01 \times 10^3 \text{ J/mol}}{22.0 \text{ J/(mol · K)}} = 273 \text{ K} = 0°C$$ Melting point of water!!

- at T>0, $\Delta G<0$: ice melting is spontaneous

- at T<0, $\Delta G>0$: ice melting is nonspontaneous

Spontaneity of Phase Changes

Phase A → Phase B

If you know the ΔH and ΔS of the phase change,

you can calculate the temperature of phase change (boiling point, melting point …)

by setting the ΔG = ΔH − TΔ S = 0

because the point of phase change is the point where the two phases are in equilibrium.

- Calculate the boiling point of Br_2 at 1 atm assuming that ΔH and ΔS are nearly temperature independent.

$$\Delta H^{\circ}_{vap} = +31.0 \text{ kJ mol}^{-1} \text{ and } \Delta S^{\circ}_{vap} = 92.9 \text{ J mol}^{-1} \text{ K}^{-1}$$

boiling point is when $l \to g$ and $g \to l$ is in equilibrium $\Delta G = 0$

Corresponding eqn : $B_2(l) \longrightarrow Br_2(g)$ ΔH°_{vap} ΔS°_{vap}

$\Delta G^{\circ}_{vap} = \Delta H^{\circ}_{vap} - T_{eq} \Delta S^{\circ} = 0$

$31.0 \text{ kJ mol}^{-1} - T_{eq} \times 92.9 \text{ J mol}^{-1} K^{-1} = 0$

$T_{eq} = \dfrac{31.0 \text{ kJ mol}^{-1}}{92.9 \text{ J mol}^{-1} K^{-1}} = \dfrac{31.0 \times 10^{3} \text{ J mol}^{-1}}{92.9 \text{ J mol}^{-1} K^{-1}} = 334 \text{ K}$

Spontaneity of Reactions vs Temperature

- For reactions,

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

- Spontaneity (ΔG) changes with temperature.
- The thermodynamic charts provide ΔH and ΔS values at 293 K at standard condition.
- The variations of ΔH and ΔS are relatively insensitive to the temperature, so we can approximate $\Delta H° = \Delta H°_{298}$ and $\Delta S° = \Delta S°_{298}$.
- Therefore,

$$\Delta G°_T = \Delta H°_{298} - T\,\Delta S°_{298}$$

- For the reaction $N_2O_4(g) \rightarrow 2\ NO_2(g)$,
- $\Delta H°_{rxn}$ = 57.9 kJ and $\Delta S°_{rxn}$ = 177 J/K at 298 K.
- What is the $\Delta G°_{rxn}$ at 105°C?

$$\Delta G°_{rxn} = \Delta H°_{rxn} - T\,\Delta S°_{rxn}$$
$$= 57.9\ kJ - 378K \times 177\ J/K \times 10^{-3}\ kJ/J$$
$$-9.01\ kJ$$

- What is the lowest temperature at which the following reaction is spontaneous?

$$H_2O(g) + C(s) \rightarrow H_2(g) + CO(g)$$
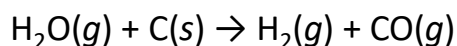
ΔH_f° -241.8 0 0 -110.5 kJ mol^{-1}

S° 188.7 5.69 130.6 197.9 J mol^{-1}K^{-1}

$\Delta H_{rxn}^\circ = 1\,mol \times (-110.5)\,kJ\,mol^{-1} - 1\,mol \times (-241.8)\,kJ\,mol^{-1} = 131.5\,kJ$

$\Delta S_{rxn}^\circ = 1\,mol \times 130.6\,J\,mol^{-1}K^{-1} + 1\,mol \times 197.9\,J\,mol^{-1}K^{-1}$
$\qquad\qquad - [1\,mol \times 188.7\,J\,mol^{-1}K^{-1} + 1\,mol \times 5.69\,J\,mol^{-1}K^{-1}] = 134.11\,J\,K^{-1}$

@ equilibrium $\Delta G = 0$ $\Delta G_{rxn}^\circ = \Delta H_{rxn}^\circ - T_{eql}\Delta S_{rxn}^\circ = 0$

$\Delta H_{rxn}^\circ = T_{eql}\Delta S_{rxn}^\circ$ $T_{eql} = \dfrac{\Delta H_{rxn}^\circ}{\Delta S_{rxn}^\circ} = \dfrac{131.5 \times 10^3\,J}{134.11\,J\,K^{-1}} = 980.5\,K$

- Above what temperature does nitrogen monoxide form from nitrogen and oxygen?

$$N_2(g) + O_2(g) \rightarrow 2\,NO(g)$$
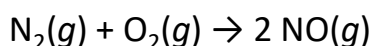
- Assume that the values of ΔH°_{rxn} and ΔS°_{rxn} do not change appreciably with temperature.

calculate from thermodynamic tables.

$\Delta H_{rxn}^\circ = 180.74\;(kJ)\,mol^{-1}$ $\Delta S_{rxn}^\circ = 24.7\;(J)\,mol^{-1}$

@ $\Delta G = 0$:   equilibrium $\Delta G = \Delta H - T\Delta S = 0$

$\Delta H = T\Delta S$ $T = \dfrac{\Delta H}{\Delta S} = \dfrac{180.74 \times 10^3\,J\,mol^{-1}}{24.7\,J\,mol^{-1}K^{-1}}$ $7317\,K$

Extensive vs. Intensive Properties

- **Extensive property**
  - A property that depends on the amount of substance
  - volume, heat capacity, mass, etc.

- **Intensive property**
  - A property that is independent of the amount of substance
  - temperature, density, pressure, specific heat, etc.

Product Rule

$$(f \cdot g)' = f' \cdot g + f \cdot g'$$

$$\frac{d}{dx}(u \cdot v) = u \cdot \frac{dv}{dx} + v \cdot \frac{du}{dx}$$

$$d(uv) = u\,dv + v\,du$$

Dependence of Gibbs Free Energy on T and P

- G = H − T S   dG = dH − T dS − S dT
- H = U + P V   dH = dU + V dP + P dV
- dU = dq + dw   1st Law
- dq$_{rev}$ = T dS   2nd Law

- Combination of 1st and 2nd laws

- **dG = V dP − S dT**   **dU = T dS − P dV**

Dependence of Gibbs Free Energy on T and P

$$dG = VdP - SdT$$

constant P

- $dG = -S\,dT$
- $\left(\dfrac{\partial G}{\partial T}\right)_P = -S$

- $\left[\dfrac{\partial\left(\frac{\Delta G}{T}\right)}{\partial T}\right]_P = -\dfrac{\Delta H}{T^2}$
- Gibbs-Helmholtz eqn.
- Temperature dependence of G

constant T

- $dG = V\,dP$
- $\left(\dfrac{\partial G}{\partial P}\right)_T = V$
- $\Delta G = \int_{P_1}^{P_2} V\,dP = \int_{P_1}^{P_2} \dfrac{nRT}{P}\,dP$
- $\Delta G = nRT\,\ln\dfrac{P_2}{P_1}$
- $G = G^\circ + nRT\,\ln\dfrac{P_2}{1\,bar}$
- $\bar{G} = \bar{G}^\circ + RT\,\ln\dfrac{P_2}{1\,bar}$
- Pressure dependence of G

A 0.590-mol sample of an ideal gas initially at 300 K and 1.50 bar is compressed isothermally to a final pressure of 6.90 bar. Calculate the change in Gibbs energy for this process.

$$\Delta G = nRT \ln \frac{P_2}{P_1} = 0.590 \text{ mol} \times 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}$$

$$\times \ln \frac{6.90 \text{ bar}}{1.50 \text{ bar}}$$

$$= 2.25 \times 10^3 \text{ J}$$

Dependence of Gibbs Free Energy on T and P

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \qquad \left(\frac{\partial G}{\partial P}\right)_T = V$$

• S>0 for all substances
  • G always decreases with temperature
  • G decreases most sharply when entropy is large

• V>0 for all substances
  • G always increases with pressure
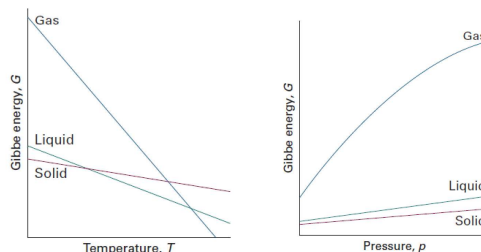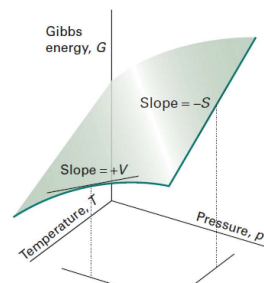
$$\Delta G = \Delta H - T \Delta S < 0 \qquad \text{Spontaneous}$$

Processes proceed in the direction of "decreasing G":
more stable in terms of Gibbs free energy

Phase Equilibria

- **Phase**: a form of matter that is uniform throughout in chemical composition and physical state
  - separated with other phases through boundaries
- If two phases are in equilibrium (boiling point, freezing point, etc.)

$$\Delta G = \bar{G}_\alpha - \bar{G}_\beta = 0$$
$$\bar{G}_\alpha = \bar{G}_\beta$$

- For example, at boiling point,

$$H_2O \ (l) \longleftrightarrow H_2O \ (g)$$

$$\Delta G = \bar{G}_{H2O(g)} - \bar{G}_{H2O(l)} = 0$$

Phase Equilibria

- $\left(\frac{\partial \bar{G}}{\partial T}\right)_P = -\bar{S}$: slope in G vs. T graph

- The slope in the G vs. T graph is -S (entropy).

- Entropy of gas is highest => gas has the most negative slope :
    - G of gas decreases fastest with temperature

- |Slope (-S)|: gas >> liquid > solid
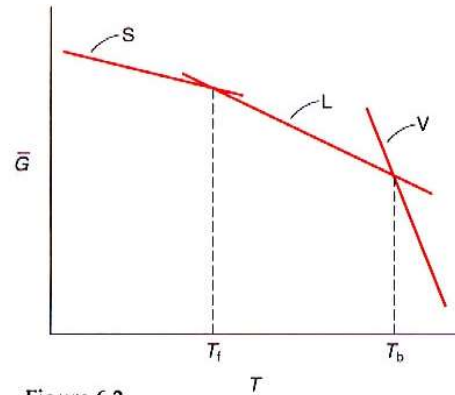
Figure 6.2

Phase Equilibria

- $\left(\frac{\partial \bar{G}}{\partial P}\right)_T = \bar{V}$: slope in G vs. P graph

- Since V>0, G always increases with pressure

- Generally, freezing point and boiling point **increases** with increasing pressure.

- Except for water ($V_{solid} > V_{liquid}$: the volume of ice is higher than water)
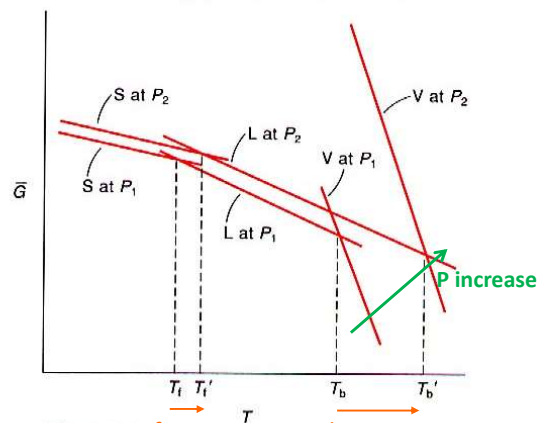
Figure 6.3   f.p. increase   b.p. increase

Lower Density of Ice than Water

- Due to the hydrogen bonding, an hexagonal lattice is formed within the solid water (ice).
- The structure has a lot of hollow volume within the structure.
- Therefore water is denser than ice.
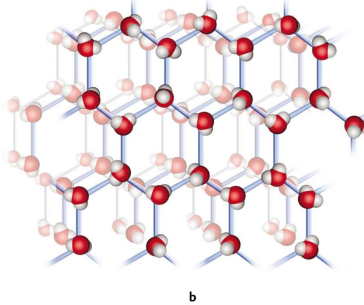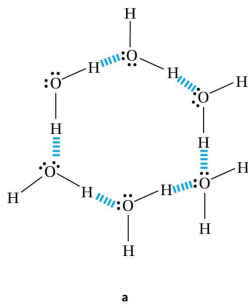
In general, the solid phase is denser than the liquid phase.
However, water is denser than ice due to the hexagonal structure formed due to the hydrogen bonding.
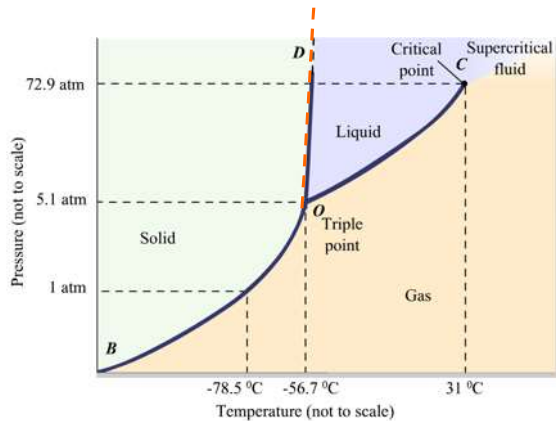
Phase Diagram : Water
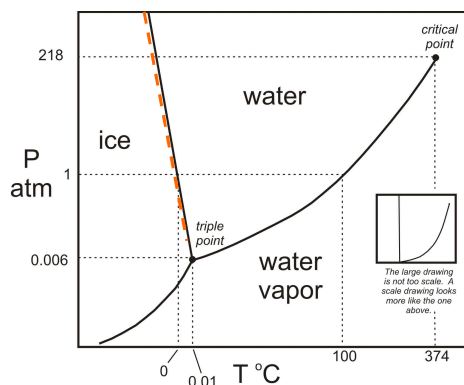
The slopes (dP/dT) are generally positive but water is an exception because the slope for solid-liquid boundary is negative due to the higher volume of ice compared to water.

- A phase diagram shows the phase of a substance at a given temperature and pressure
- X axis : temperature, Y axis : pressure
- **Triple point**: The temperature and pressure at which all three phases s, l, and g exist in equilibrium

- The boiling point of water at 1 atm is 100°C, freezing point is 0°C.
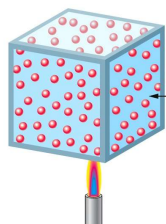
Phase Diagram : CO_2

- The slope for solid-liquid boundary is positive, like all other boundaries, following the general trend.

- CO_2 sublimates from solid to gas at atmospheric pressure: it does not exist as liquid at atmospheric pressure.

Phase Diagrams
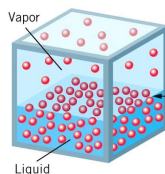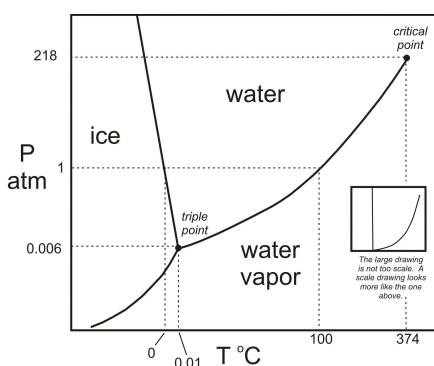
- **Critical Point** (critical temperature T_c and critical pressure P_c):

- the highest temperature and pressure where the liquid and gas phase are separated by a interface

- Liquid and gas densities become equal after the critical point.

- The phase takes on intermediate properties of gas and liquid.

The substance is called a **supercritical fluid** after the critical point.

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Supercritical Fluids

- Excellent solvents
- Supercritical fluid of CO_2: used for decaffeination of coffee

Andy Washnik

https://youtu.be/GEr3NxsPTOA

Phase Equilibria

- Two phases **α and β** are in equilibrium:

- $\bar{G}_\alpha = \bar{G}_\beta$

$d\bar{G} = \bar{V}dP - \bar{S}dT$

- $d\bar{G}_\alpha = d\bar{G}_\beta$ ⟵

$d\bar{G}_\alpha = \bar{V}_\alpha dP - \bar{S}_\alpha dT$
$d\bar{G}_\beta = \bar{V}_\beta dP - \bar{S}_\beta dT$

- $\bar{V}_\alpha dP - \bar{S}_\alpha dT = \bar{V}_\beta dP - \bar{S}_\beta dT$

- $(\bar{S}_\beta - \bar{S}_\alpha)dT = (\bar{V}_\beta - \bar{V}_\alpha)dP$

at equilibrium,

$\Delta G = \Delta H - T\Delta S = 0$

- $\dfrac{dP}{dT} = \dfrac{\Delta\bar{S}}{\Delta\bar{V}}$ ⟵

$\Delta S = \Delta\bar{H}/T$

- $\boldsymbol{\dfrac{dP}{dT} = \dfrac{\Delta\bar{H}}{T\Delta\bar{V}}}$

Clapeyron equation
(general equation for equilibrium between any phases)

Phase Equilibria

Equilibrium between liquid/solid and gas (vaporation)

liquid/solid $\longleftrightarrow$ gas

- $\dfrac{dP}{dT} = \dfrac{\Delta \bar{H}}{T \Delta \bar{V}}$ $\longleftarrow$ $\Delta \bar{H} = \Delta_{vap} \bar{H}$

  $\Delta \bar{V} = \Delta_{vap} \bar{V} = \bar{V}_{vap} - \bar{V}_{liquid} \approx \bar{V}_{vap} = \dfrac{RT}{P}$
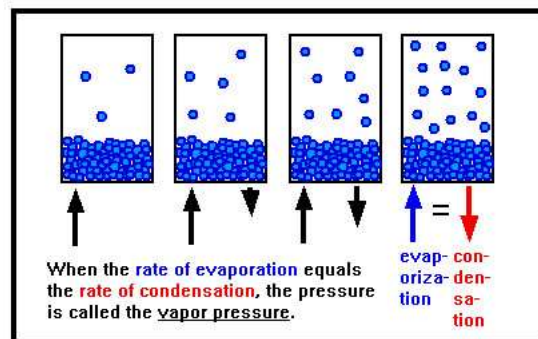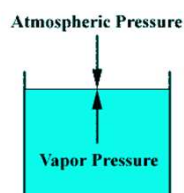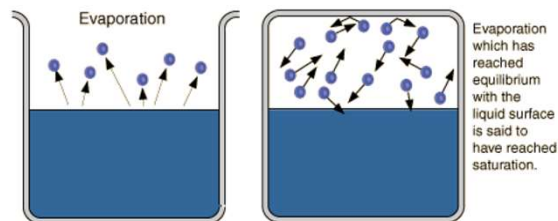
- $\dfrac{dP}{dT} = \dfrac{P \, \Delta_{vap} \bar{H}}{RT^2}$

- $\dfrac{dP}{P} = \dfrac{\Delta_{vap} \bar{H}}{RT^2} dT$ **Clausius-Clapeyron equation**
  (for evaporation, sublimation)

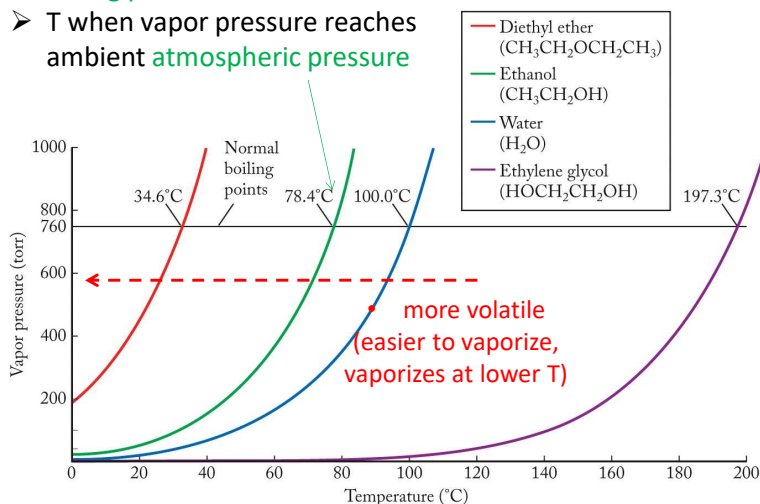- $\boldsymbol{\ln P = -\dfrac{\Delta_{vap} \bar{H}}{RT} + const}$ $\ln \dfrac{P_2}{P_1} = \dfrac{\Delta_{vap} \bar{H}}{RT} \dfrac{(T_2 - T_1)}{T_1 T_2}$

Vapor Pressure

- T increase => vapor pressure increases
- Boiling point:
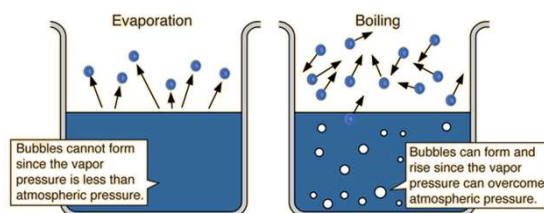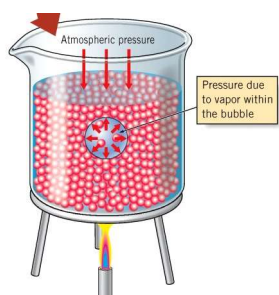- ➤ T when vapor pressure reaches ambient atmospheric pressure

normal boiling point: at 1 atm

Diethyl ether $(CH_3CH_2OCH_2CH_3)$
Ethanol (CH_3CH_2OH)
Water (H_2O)
Ethylene glycol $(HOCH_2CH_2OH)$

Normal boiling points

34.6°C   78.4°C   100.0°C   197.3°C

more volatile
(easier to vaporize, vaporizes at lower T)

- The *lower* the intermolecular attraction, the easier to vaporize,
- ➤ the higher the vapor pressure
- ➤ the lower the boiling point

At the boiling point (temperature),

Vapor Pressure = Atmospheric Pressure

Atmospheric pressure

Pressure due to vapor within the bubble

Evaporation   Boiling

Bubbles cannot form since the vapor pressure is less than atmospheric pressure.

Bubbles can form and rise since the vapor pressure can overcome atmospheric pressure.

Clausius-Clapeyron Equation

P_{vap} vs T

- $\ln(P_{vap}) = -\dfrac{\Delta H_{vap}}{R}\left(\dfrac{1}{T}\right) + C$

  y   =   a   x   + b

➢ ln(P_{vap}) vs. (1/T) : linear

➢ slope a = $-\dfrac{\Delta H_{vap}}{R}$ => determine ΔH_{vap}

➢ $\Delta H_{vap} = -$slope a $\times R$

The unit of the slope is K.

ln(P_{vap}) vs 1/T