화학 General Chemistry
034.020-005

2018 Spring Semester

Tue/Thr 9:30~10:45
Building 028-302
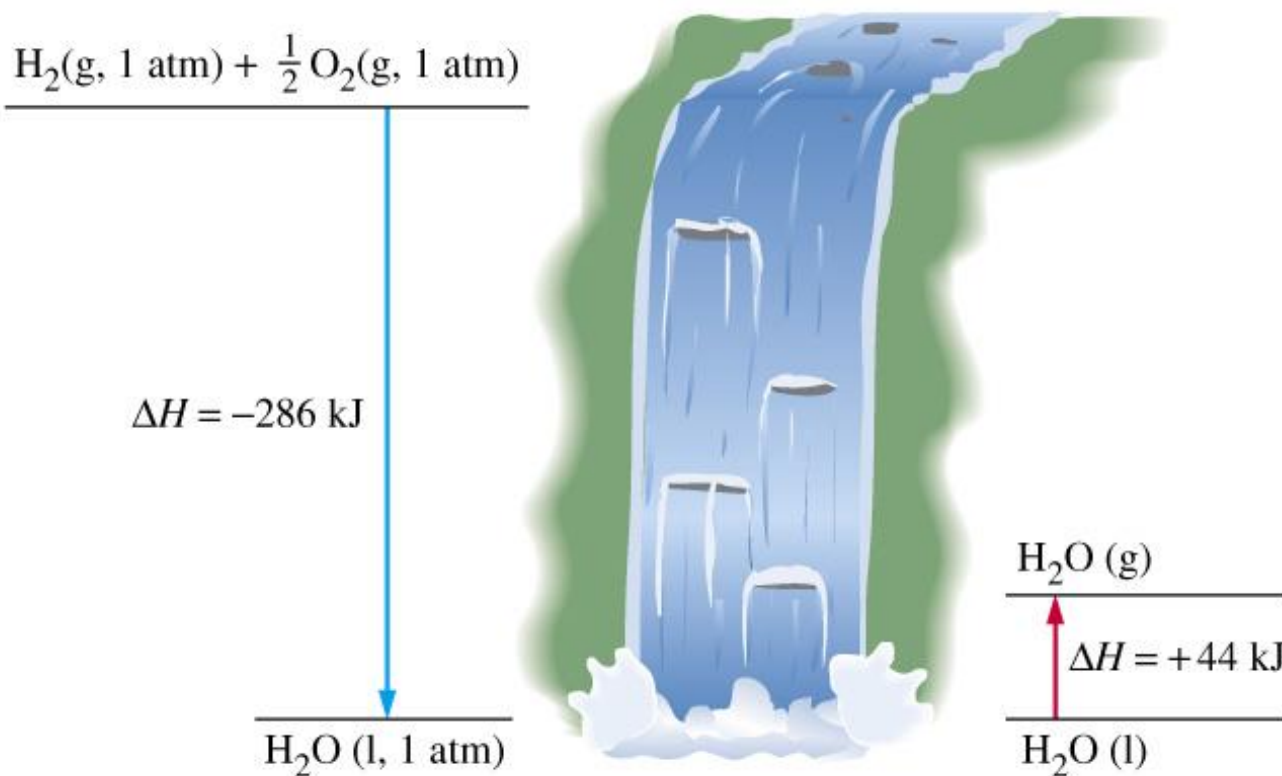
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Entropy
8.1. Spontaneous Change

- The 1st **law** of thermodynamics

- The **directionality** of physical or chemical changes?

- Spontaneous change: a change that has a tendency to occur w/o
needing to be driven an external influence.

Direction of decreasing energy:
Is it a criterion for spontaneous change?

$H_2(g, 1\ atm) + \frac{1}{2}O_2(g, 1\ atm)$

$\Delta H = -286\ kJ$

$H_2O\ (l, 1\ atm)$

The formation of water at 25 °C
and 1 atm: a spontaneous process
that is exothermic

$H_2O\ (g)$

$\Delta H = +44\ kJ$

$H_2O\ (l)$

The vaporization of water at 25 °C and
pressures up to 0.0313 atm: a spontaneous
process that is endothermic

Exothermic, Spontaneous

Endothermic, Spontaneous

Examples

- $H_2O(s) \rightarrow H_2O(l)$: ΔH= +6 kJ/mole (Endothermic, yet spontaneous)

- A ball rolls down a hill but never spontaneously rolls back up the hill.

- Two gases mix spontaneously, but they never 'de-mix' by themselves.

SOME PROCESSES HAVE DIRECTIONALITY !!!

What Is Missing In Enthalpy?

- The 1st law of thermodynamics is not enough to explain spontaneous process.
  - Energy is conserved both in forward and backward direction.

- Enthalpy change CAN NOT TELL you the directionality of the chemical reaction!

We need another function that tells us spontaneity

Statistics and Spontaneous Change

Consider free expansion of ideal gas at const T:
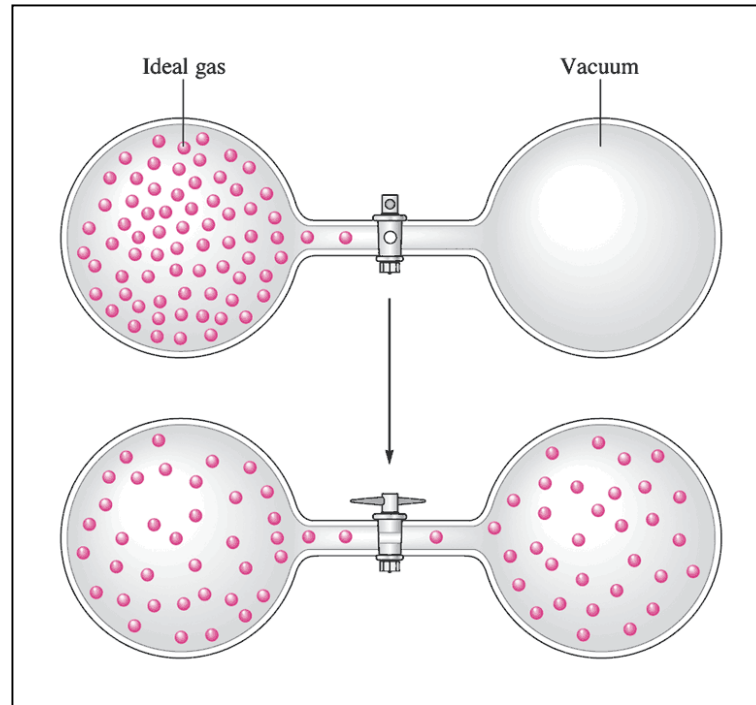
$\Delta U = 0$, $w = 0$, $q = 0$, $\Delta H = 0$

Gas spontaneously expands to fill all of the bulb volume. Why?

8.2. Entropy and Disorder

- Energy and matter tend to **disperse** in a **disorderly** fashion.

- **Entropy (S): a measure of disorder**

- **The 2nd law of thermodynamics:**

  The S of an isolated system increases in any spontaneous change.

- Dependent upon the reaction path: IT IS A **PATH** FUNCTION: q (heat), w(work)

- Independent on the reaction path: IT IS A **STATE** FUNCTION: Internal energy, Enthalpy, Entropy

Thermodynamic Entropy

- Entropy change of the system ΔS_{sys} is defined as:

$$\Delta S_{sys} = \frac{q_{sys,rev}}{T} \text{ (Joule / Kelvin)}$$

$q_{rev,sys}$: heat exchanged in a reversible manner between the system and surr

More examples:

- $S[CO_2(s)] < S[CO_2(g)]$: one mole of $CO_2(g)$ can occupy more volume→ more random.

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

- 1 mole of N_2 gas with 0.5 liter

  vs

  1 mole of N_2 gas with 10 liter

  → 10 liter gas has more volume
  → Higher entropy for larger volume.

Solid sugar is added to water to form a solution. $\Delta S_{sys} > 0$

Iodine vapor condenses on a cold surface to form crystals.

$$\Delta S_{sys} < 0$$

8.3. Changes in Entropy

- **Thermal** disorder: arising from the thermal motion of molecules
  ex) heating; KE increases; ΔS increases

- **Positional** disorder: related to the locations of the molecules
  ex) mixing with other molecules or increase in volume; ΔS increases

- Entropy change (ΔS) for heating or cooling process

For ideal gas, **const. volume**, $\quad \Delta S_{sys} = nC_v \int_{T_i}^{T_f} \dfrac{dT}{T} = nC_v \ln \dfrac{T_f}{T_i}$

For ideal gas, **const. pressure**, $\Delta S_{sys} = nC_p \ln \dfrac{T_f}{T_i}$

8.3. Changes in Entropy

- For a **reversible** and **isothermal expansion** of an **ideal gas,**

U = Potential E(=0 for
ideal gas) + Kinetic E
(dependent on T)

$$\Delta S_{sys} = \int_{V_i}^{V_f} \frac{dq_{sys,rev}}{T} = \frac{1}{T} \int_{V_i}^{V_f} dq_{sys,rev} = \frac{q_{sys,rev}}{T} = +nR \ln\left(\frac{V_f}{V_i}\right)$$

$$\Delta S_{surr} = \int_{V_i}^{V_f} \frac{dq_{surr,rev}}{T} = \frac{-q_{sys,rev}}{T} = -nR \ln\left(\frac{V_f}{V_i}\right)$$

$$\Delta S_{tot} = \Delta S_{sys} + \Delta S_{surr} = 0$$

Entropy of the universe and 2ⁿᵈ law of thermodynamics

- Entropy change of the universe:

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

2ⁿᵈ law of thermodynamics:

$$\Delta S_{univ} \geq 0$$

1. In a reversible process, the total entropy of the universe is unchanged.

$$\Delta S_{univ} = 0$$

2. In a irreversible process, the total entropy of the universe must increase.

$$\Delta S_{univ} > 0$$

3. In any case, entropy of the universe never decreases.

8.4. ΔS Accompanying Changes in Physical State

- Entropy change with phase transition

$$\boxed{\Delta H_{sys} = q \text{ (const P)}}$$

$$\Delta S_{vap} = \frac{q_{rev}}{T_b} = \frac{\Delta H_{vap}}{T_b} > 0 \qquad \Delta S_{fus} = \frac{\Delta H_{fus}}{T_f} > 0$$

- **Trouton's rule**: $\Delta S_{vap}{}^o \approx 85\ J \cdot mol^{-1} \cdot K^{-1}$

| Liquid	Boiling point (K)	$\Delta S_{vap}°$ (J·K^{-1}·mol^{-1})
acetone	329.4	88.3
ammonia	239.7	97.6
argon	87.3	74
benzene	353.2	87.2
ethanol	351.5	124
helium	4.22	20.
mercury	629.7	94.2
methane	111.7	73
methanol	337.8	105
water	373.2	109

More ordered in liquid state
Less ordered in liquid state

*The normal boiling point is the boiling temperature at 1 atm.

Various kind of inter-molecular forces (in Chapter5)

: **much weaker** than the covalent or ionic chemical bonding, yet strong enough to influence the physical properties.

Type of interaction	Typical energy (kJ·mol^{-1})
ion–ion	250
ion–dipole	15
dipole–dipole	2
	0.3
dipole–induced-dipole	2
London (dispersion)†	2
hydrogen bonding	20
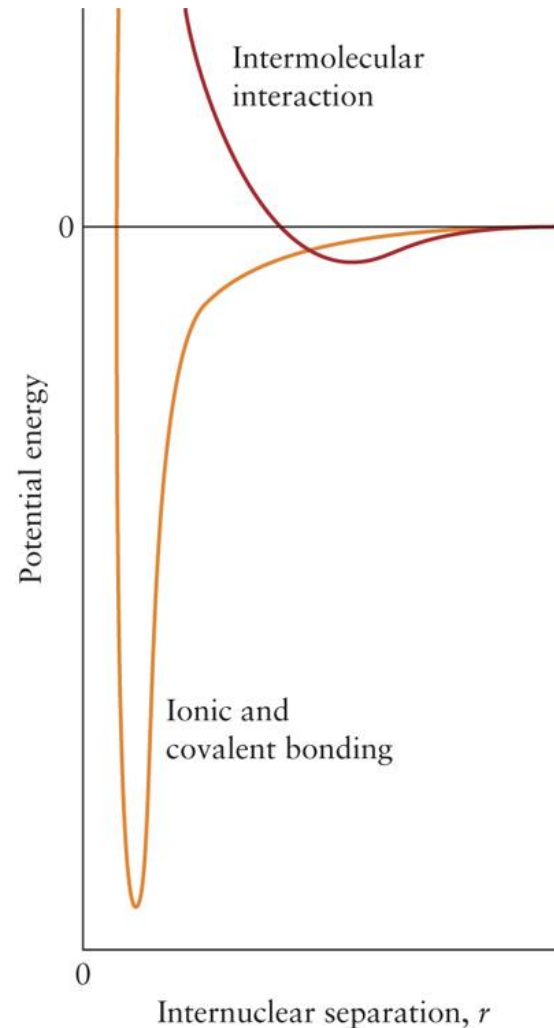
The 3rd Law: The entropy of a perfect crystal at 0K is zero.

The entropy of any substance (element or compound) approaches zero at T = 0.

S (T = 0) = 0 J/K for ALL pure substance.

→The absolute values of entropy can be defined !!!!

T=0 K, S = 0   T > 0 K, S > 0
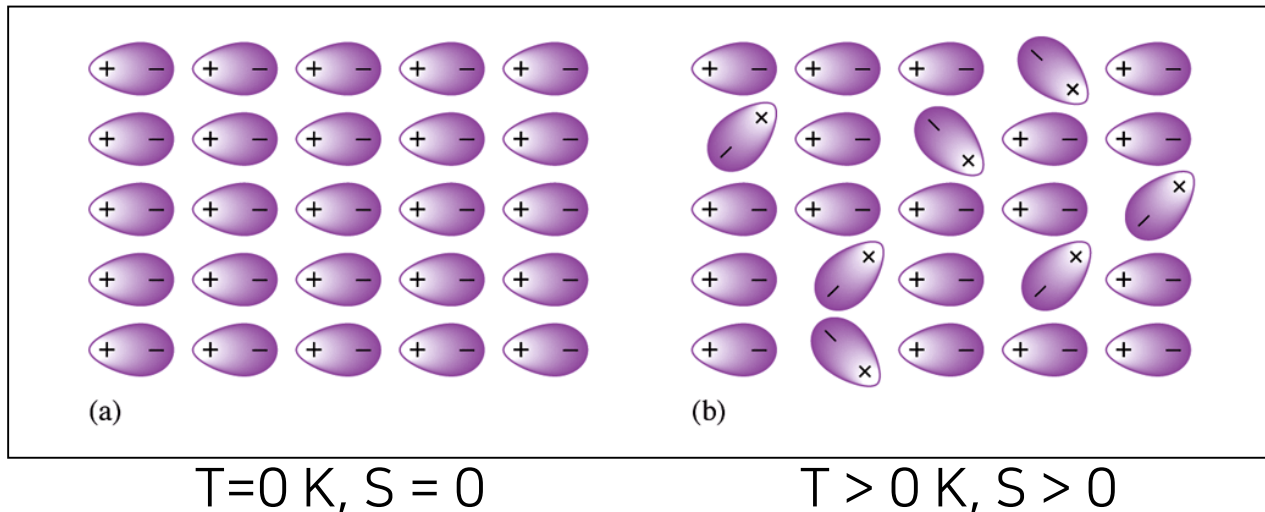
8.5. A Molecular Interpretation of Entropy

- The 3rd law of thermodynamics

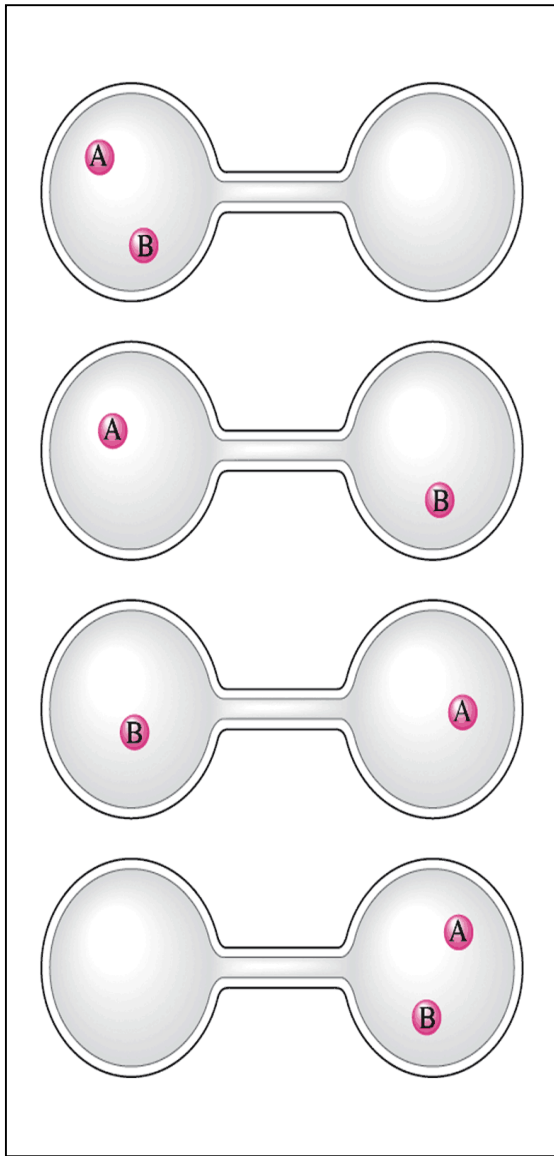 The S of all perfect crystals approach zero as T (K) → 0.

- **Boltzmann formula** (statistical entropy)

  k_B: Boltzmann constant = 1.37 x 10^{-27} J K^{-1}

  W : the number of ways that the atoms or molecules in the

  sample can be arranged and yet still give rise to the same

  total energy (the number of micro-states)

- W approaches zero as T → 0 for perfect crystals.

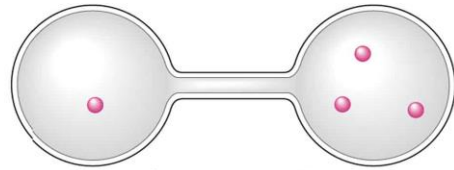| Number of possible combinations	Probability
1	1/4
2	1/2
1	1/4

Number of possible combinations

Arrangement I
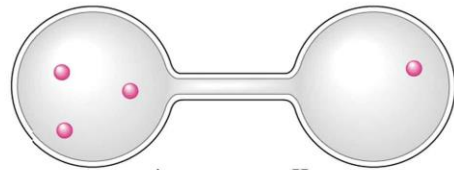
Arrangement II

Arrangement III

Arrangement IV

Arrangement V

TABLE 16.1 The Microstates That Give a Particular Arrangement (State)

Arrangement	Microstates	No. of Ways	Probability
			LEAST PROBABLE
I		1	1/16
II		4	1/4
III			MOST PROBABLE
		6	3/8
IV		4	1/4
			LEAST PROBABLE
V		1	1/16

Now suppose we have 10^{23} number of molecules···.

TABLE 16.2 Probability of Finding All the Molecules in the Left Bulb as a Function of the Total Number of Molecules

Number of Molecules	Relative Probability of Finding All Molecules in the Left Bulb
1	$\dfrac{1}{2}$
2	$\dfrac{1}{2} \times \dfrac{1}{2} = \dfrac{1}{2^2} = \dfrac{1}{4}$
3	$\dfrac{1}{2} \times \dfrac{1}{2} \times \dfrac{1}{2} = \dfrac{1}{2^3} = \dfrac{1}{8}$
5	$\dfrac{1}{2} \times \dfrac{1}{2} \times \dfrac{1}{2} \times \dfrac{1}{2} \times \dfrac{1}{2} = \dfrac{1}{2^5} = \dfrac{1}{32}$
10	$\dfrac{1}{2^{10}} = \dfrac{1}{1024}$
n	$\dfrac{1}{2^n} = \left(\dfrac{1}{2}\right)^n$
6×10^{23} (1 mole)	$\left(\dfrac{1}{2}\right)^{6 \times 10^{23}} \approx 10^{-(2 \times 10^{23})}$

- Gas in a bulb SPONTANEOUSLY expands because⋯
  it is the most probable configuration.

- Gas NEVER compresses itself because⋯
  it is highly (statistically) improbable.

- System "spontaneously"
  changes to the (microscopically) most probable state!!!!

- Most probable state
  = most random configuration

8.5-6. A Molecular Interpretation of Entropy

- The 3rd law of thermodynamics

The S of all perfect crystals approach zero as T (K) → 0.

- Boltzmann formula (statistical entropy)

W : the number of ways that the atoms or molecules in the sample can be arranged and yet still give rise to the same total energy (the number of micro-states)

- W approaches zero as T → 0 for perfect crystals.
- Statistical entropy
- If there is only one microstate, **ln1 = 0; therefore S=0**

8.7. Standard Molar Entropies

$$S(T) = S(0) + \Delta S\,(0K \to T) = \Delta S\,(0K \to T)$$

$$S(T) = S(0) + \int_0^T \frac{dq_{rev}}{T} = \int_0^T \frac{C}{T}\,dT \qquad dS = \frac{q_{rev}}{T} = \frac{C\,dT}{T}$$

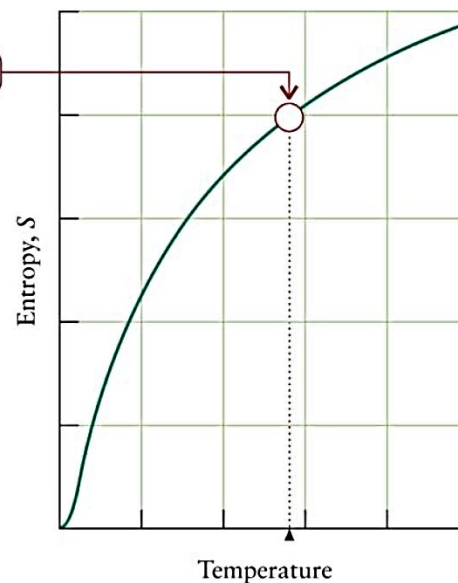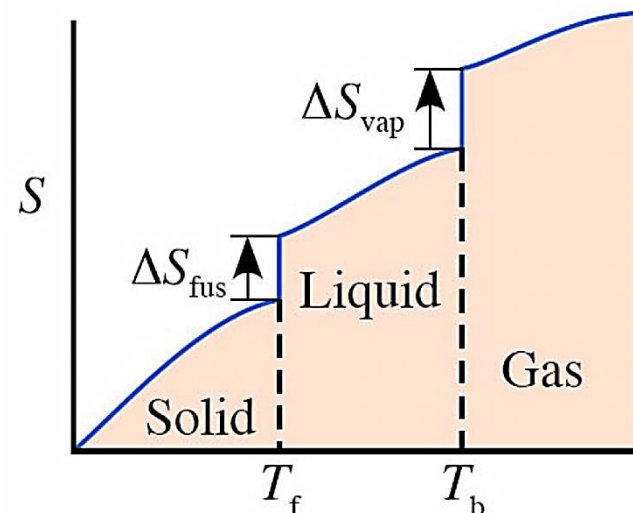$$S(T) = \int_0^T \frac{C_P}{T}\,dT \qquad (at\ constant\ P)$$

C_P and $C_P/T \to 0$ as $T \to 0$

Area

(a) Heat capacity, C_P — Temperature

(b) C_P/T — Temperature

(c) Entropy, S — Temperature
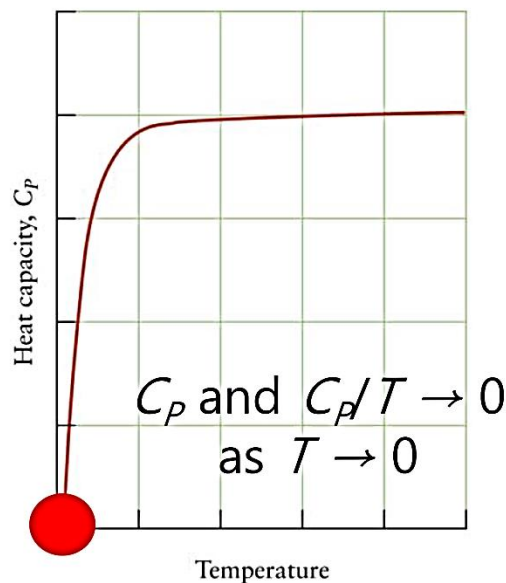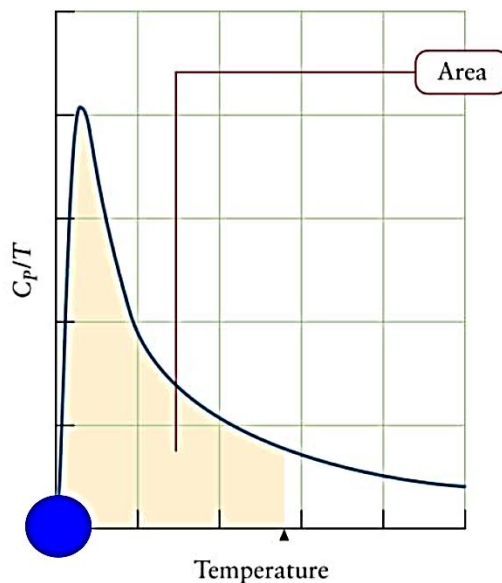
- More precisely,

$$S(T) = \int_0^T \frac{C_P}{T}\, dT + \sum \Delta S_{phase} \quad (at\ const\ P)$$

Gases	S_m°	Liquids	S_m°	Solids	S_m°
ammonia, NH_3	192.4	benzene, C_6H_6	173.3	calcium oxide, CaO	39.8
carbon dioxide, CO_2	213.7	ethanol, C_2H_5OH	160.7	calcium carbonate, $CaCO_3^\dagger$	92.9
hydrogen, H_2	130.7	water, H_2O	69.9	diamond, C	2.4
nitrogen, N_2	191.6			graphite, C	5.7
oxygen, O_2	205.1			lead, Pb	64.8

Q) Without calculation, can you estimate the sign of entropy change in the following reactions?
(a) $N_2\ (g)+ 3H_2(g) \rightarrow 2NH_3\ (g)$ (b) $CaCO_3(s) \rightarrow CaO(s) +CO_2(g)$
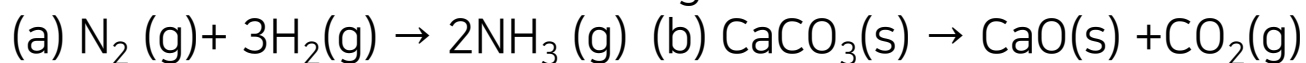
Global Changes in Entropy
8.8. The Surroundings
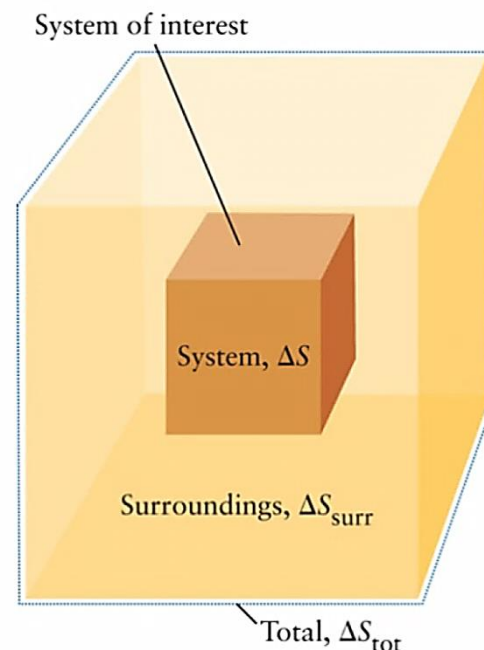
$$\Delta S_{tot} = \Delta S_{sys} + \Delta S_{surr}$$

- Only if the $\Delta S_{tot} > 0$ the process will be spontaneous.

$$\Delta S_{surr} = \frac{q_{surr,rev}}{T_{surr}} = \frac{-q_{sys,rev}}{T_{surr}}$$

$$\Delta S_{surr} = \frac{-\Delta H_{sys}}{T_{surr}} \; (at \; const \; P)$$

Exothermic reaction ($\Delta H_{sys} < 0$): $\Delta S_{surr} > 0$

Endothermic reaction ($\Delta H_{sys} > 0$): $\Delta S_{surr} < 0$

System of interest

System, ΔS

Surroundings, ΔS_{surr}

Total, ΔS_{tot}

Example: Calculate the entropy change of **surrounding** when water freeze to ice at 263 K. Use $\Delta H_{fus} = 6.0 \; kJ \cdot mol^{-1}$ at 263K. ($\Delta S_{fus} \approx 22 \; J \cdot mol^{-1}$)
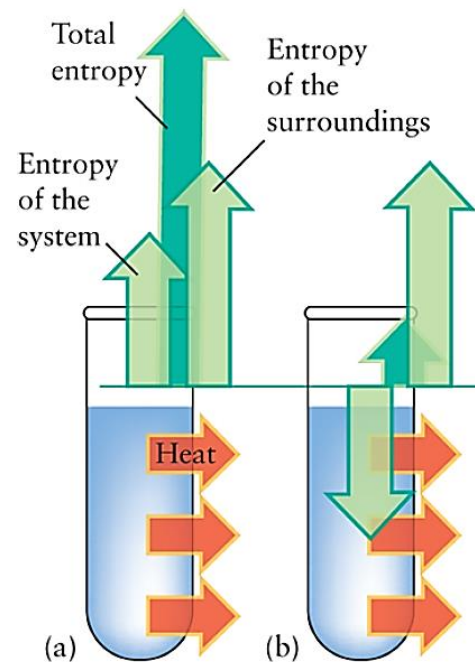
8.9. The Overall Change in Entropy
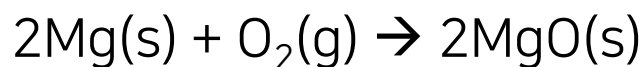# 8.10. Equilibrium

$\Delta S_{tot} > 0 \rightarrow$

$\Delta S_{tot} = 0 \rightarrow$

$\Delta S_{tot} < 0 \rightarrow$

Total entropy

Entropy of the surroundings

Entropy of the system

Heat

(a)   (b)

Example

Spontaneous reaction or not at standard state and 298 K

2Mg(s) + O_2(g) → 2MgO(s) $\Delta S^o = -217\ J \cdot K^{-1}$ $\Delta H^o = -1202\ kJ$

ΔS_{sys} $\Delta S_{surr} = \dfrac{-\Delta H_{sys}}{T_{surr}}\ (\textit{at const } P)$

- Spontaneous endothermic reactions:

There can still be an overall increase in entropy if
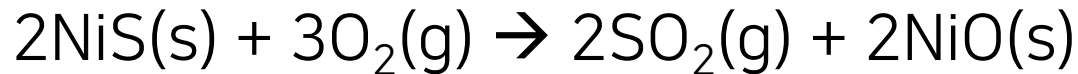
the disorder of the system increases enough.

Entropy of the system

Total entropy

Heat

Entropy of the surroundings
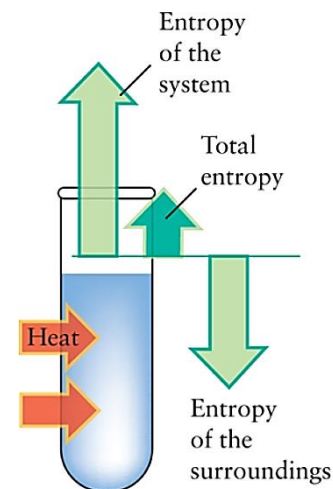
ΔS	ΔS_{surr}	ΔS_{tot}	Character
>0	>0	>0	spontaneous
<0	<0	<0	not spontaneous; reverse change is spontaneous
>0	<0		spontaneous if ΔS is greater than $-\Delta S_{surr}$
<0	>0		spontaneous if ΔS_{surr} is greater than $-\Delta S$

Standard State Entropy Values, S^o (1 atm) and Entropy change of chemical reaction

$$\Delta S^0_{rxn} = \sum n_p S^0_{products} - \sum n_r S^0_{reactants}$$

Calculate ΔS^o at 298 K for the reaction:

$$2NiS(s) + 3O_2(g) \rightarrow 2SO_2(g) + 2NiO(s)$$

Substance	S^o(J/K.mol)
SO2(g)	248
NiO(s)	38
O_2(g)	205
NiS(s)	53

$\Delta S = 2 \times S_{SO2} + 2 \times S_{NiO} - 2 \times S_{NiS} - 3 \times S_{O2}$

$= 2 \times 248 + 2 \times 38 - 2 \times 53 - 3 \times 205$

$= -149$ J/K.mol

Gibbs Free Energy
8.11. Focusing on the System

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

$$\Delta S_{tot} = \Delta S_{sys} + \Delta S_{surr} = \Delta S_{sys} + \frac{-\Delta H_{sys}}{T} = \frac{-(\Delta H_{sys} - T\Delta S_{sys})}{T}$$
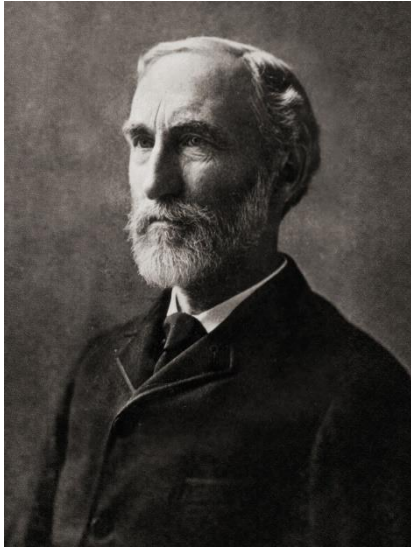
$$\Delta S_{tot} = \frac{-\Delta(H_{sys} - TS_{sys})}{T} = \frac{-\Delta G_{sys}}{T} \quad (at\ constant\ T\ and\ P)$$

$$G \equiv H - TS$$

$\Delta G < 0$ → spontaneous, irreversible

$\Delta G = 0$ → reversible or equilibrium

$\Delta G > 0$ → nonspontaneous

Josiah Willard Gibbs (1839 –1903)

Initially unaware of Gibbs's contributions in that field, Albert Einstein wrote three papers on statistical mechanics, published between 1902 and 1904. After reading Gibbs's textbook (which was translated into German in 1905), Einstein declared that Gibbs's treatment was superior to his own and explained that he would not have written those papers if he had known Gibbs's work

The Gibbs free energy, originally called *available energy*, was developed in the 1870s by the American scientist Josiah Willard Gibbs.

In 1873, Gibbs described this "available energy" as

"the **greatest amount of mechanical work** which can be obtained from a given quantity of a certain substance in a given initial state, without increasing its total volume or allowing heat to pass to or from external bodies, except such as at the close of the processes are left in their initial condition."

| Enthalpy change	Entropy change	Spontaneous?
exothermic ($\Delta H < 0$)	increase ($\Delta S > 0$)	yes, $\Delta G < 0$
exothermic ($\Delta H < 0$)	decrease ($\Delta S < 0$)	yes, if $\left|T\Delta S\right| < \left|\Delta H\right|, \Delta G < 0$
endothermic ($\Delta H > 0$)	increase ($\Delta S > 0$)	yes, if $T\Delta S > \Delta H, \Delta G < 0$
endothermic ($\Delta H > 0$)	decrease ($\Delta S < 0$)	no, $\Delta G > 0$

Example

Calculate the change in molar Gibbs free energy, ΔG_m, for the process H$_2$O(s) → H$_2$O(l) at 1 atm and (a) 283 K; (b) 273 K. Decide for each T whether melting is spontaneous or not. Treat $\Delta H_{fus} = 6.01 \ kJ \cdot mol^{-1}$ and $\Delta S_{fus} = 22.0 \ J \cdot mol^{-1} \cdot K^{-1}$ as independent of T.

- G **decreases** as its T is raised at constant P.

$$G = H - TS$$

- $S(vapor) > S(liquid) > S(solid)$

    → decreasing rate $G(vapor) > G(liquid) > G(solid)$
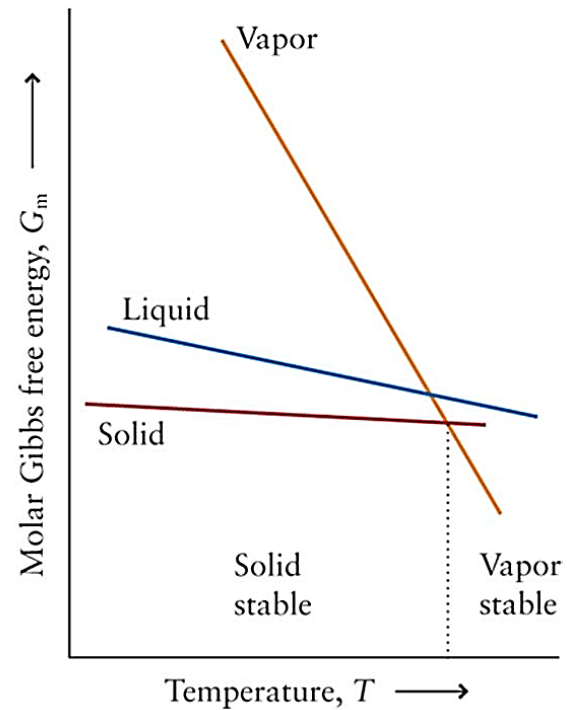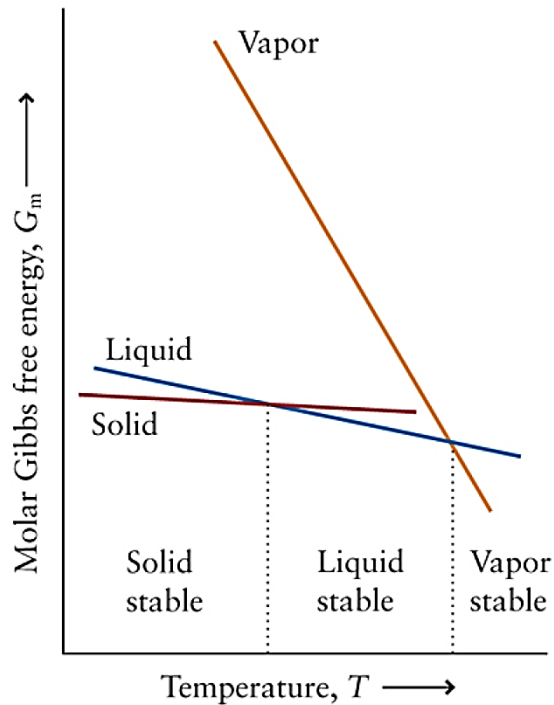
Gibbs Free Energy: $H_2O(s) \rightarrow H_2O(liq)$

The direction of chemical reaction is determined by the H and S.

$$\Delta H^o = +6.03 \text{ kJ/mol}, \quad \Delta S^o = 22.1 \text{ JK}^{-1}\text{mol}$$

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

TABLE 16.4 Results of the Calculation of ΔS_{univ} and ΔG° for the Process $H_2O(s) \rightarrow H_2O(l)$ at $-10°C$, $0°C$, and $10°C^*$

T (°C)	T (K)	$\Delta H°$ (J/mol)	$\Delta S°$ (J/K · mol)	$\Delta S_{surr} = -\dfrac{\Delta H°}{T}$ (J/K · mol)	$\Delta S_{univ} = \Delta S° + \Delta S_{surr}$ (J/K · mol)	$T\Delta S°$ (J/mol)	$\Delta G° = \Delta H° - T\Delta S°$ (J/mol)
−10	263	6.03×10^3	22.1	−22.9	−0.8	5.81×10^3	$+2.2 \times 10^2$
0	273	6.03×10^3	22.1	−22.1	0	6.03×10^3	0
10	283	6.03×10^3	22.1	−21.3	+0.8	6.25×10^3	-2.2×10^2

Spontaneous Reaction!!!

Free Energy and Chemical Reactions

- ## Standard molar Free Energy Change:
  the change in free energy that will occur if the reactants in their standard states are converted to the products in their standard states.
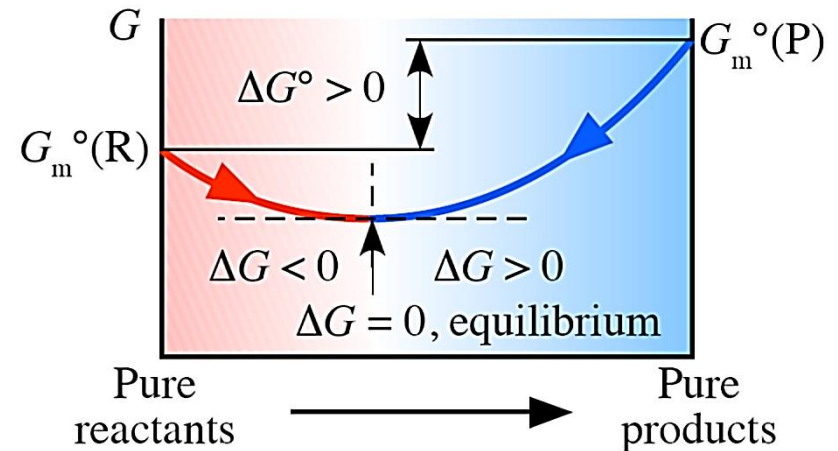
Method 1: From the standard state enthalpy and entropy changes:

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

Method 2: From the standard free energy of formation

$$\Delta G^0 = \sum n_p \Delta G^0_{f,\ products} - \sum n_r \Delta G^0_{f,\ reactants}$$

8.12. Gibbs Free Energy of Reaction

- Standard Gibbs free energy of formation ($\Delta G_f{}^o$)

: ΔG^o per mole for the formation of a compound from its elements
in their most stable form

$$\Delta G_f{}^o = n\Delta H_f{}^o - T\left(\sum nS^o(prod) - \sum nS^o(react)\right)$$

$$\Delta H^o = H^o(product) - H^o(reactant)$$

$$\Delta S^0_{rxn} = \sum n_p S^0_{\text{products}} - \sum n_r S^0_{\text{reactants}}$$

$$\Delta G_f{}^o = n\Delta H_f{}^o - T\left(\sum nS^o(prod) - \sum nS^o(react)\right)$$

$$\Delta G^0 = \sum n_p \Delta G^0_{\text{f, products}} - \sum n_r \Delta G^0_{\text{f, reactants}}$$
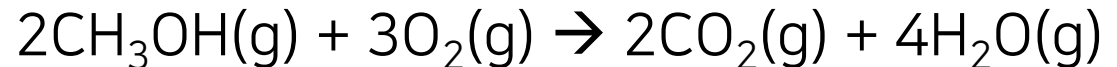
ΔH: Exothermic/Endothermic

ΔG: Exergonic/Endergonic

Example: Calculating ΔG^o :Using the free energy of formation

Substance	DG^o_f(kJ/mol)
$CH_3OH(g)$	-163
$O_2(g)$	0
$CO_2(g)$	-394
$H_2O(g)$	-229

Using the free energy of formation, calculate the DG^o for the reaction

$$2CH_3OH(g) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(g)$$

$$\Delta G^0 = \sum n_p \Delta G^0_{f,\ products} - \sum n_r \Delta G^0_{f,\ reactants}$$

$$= 2\Delta G^o_f(CO_2) + 4\Delta G^o_f(H_2O) - 2\Delta G^o_f(CH_3OH) - 3\Delta G^o_f(O_2)$$

$$= -1378 \text{ kJ/mole} \quad (< 0 : \text{spontaneou s reaction})$$

8.13. ΔG and Non-expansion Work

At constant T and P

For a Reversible change,

- For Example,
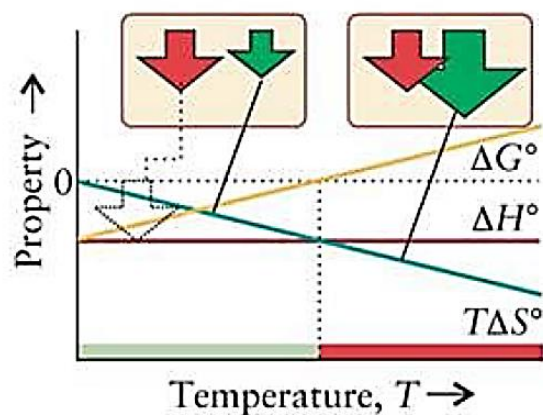
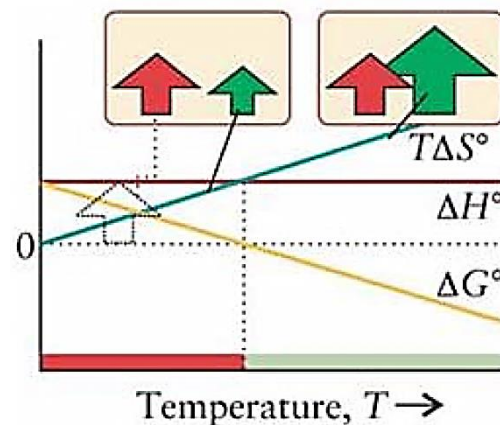$$C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l) \qquad \Delta G^o = -2879 \ kJ$$
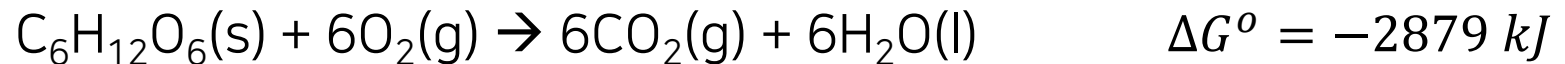
With the oxidation of 1 mol glucose, 2879 kJ of work such as making peptide bonds can be done.

8.14. The Effect of Temperature

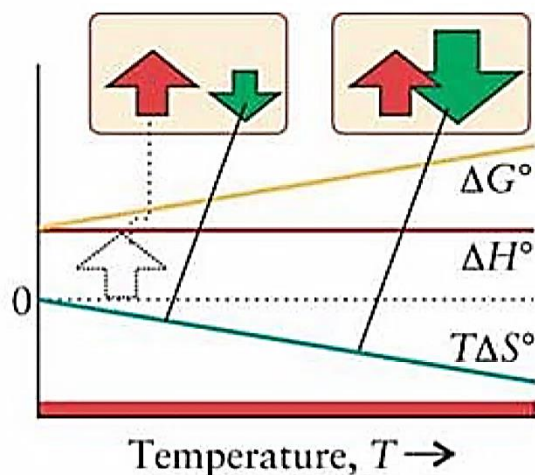- Temperature dependence of $\Delta G^o = \Delta H^o - T\Delta S^o$

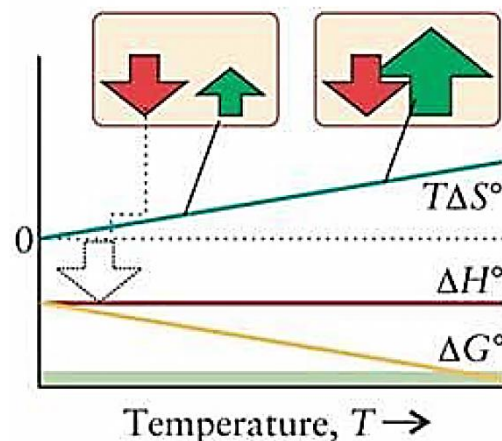(a) $\Delta H° < 0$ $\Delta S° < 0$

(b) $\Delta H° > 0$ $\Delta S° > 0$

(c) $\Delta H° > 0$ $\Delta S° < 0$

(d) $\Delta H° < 0$ $\Delta S° > 0$

8.15. Impact on Biology: Gibbs Free Energy Changes in Biological Systems

- A reaction that produces a lot of **entropy** can

drive another nonspontaneous reaction forward.

- A process may be driven uphill in Gibbs free

energy by another reaction that rolls **downhill**.

ATP $\rightleftarrows$ ADP + Pi $\Delta G^o = -30$ kJ

Apparently spontaneous

Spontaneous