Thermodynamic

Second year/Second semester

<u>Entropy Changes and the Third Law of Thermodynamics</u>

Entropy (S) is a thermodynamic property of all substances that is proportional to their degree of disorder. The greater the number of possible microstates for a system, the greater the disorder and the higher the entropy.

The atoms, molecules, or ions that compose a chemical system can undergo several types of molecular motion, including translation, rotation, and vibration (Figure 1 "Molecular Motions"). The greater the molecular motion of a system, the greater the number of possible microstates and the higher the entropy. A perfectly ordered system with only a single microstate available to it would have an entropy of zero. The only system that meets this criterion is a perfect crystal at a temperature of absolute zero (0 K), in which each component atom, molecule, or ion is fixed in place within a crystal lattice and exhibits no motion.. In practice, absolute zero is an ideal temperature that is unobtainable, and a perfect single crystal is also an ideal that cannot be achieved. Nonetheless, the combination of these two ideals constitutes the basis for the third law of thermodynamics: *the entropy of any perfectly ordered, crystalline substance at absolute zero is zero*.
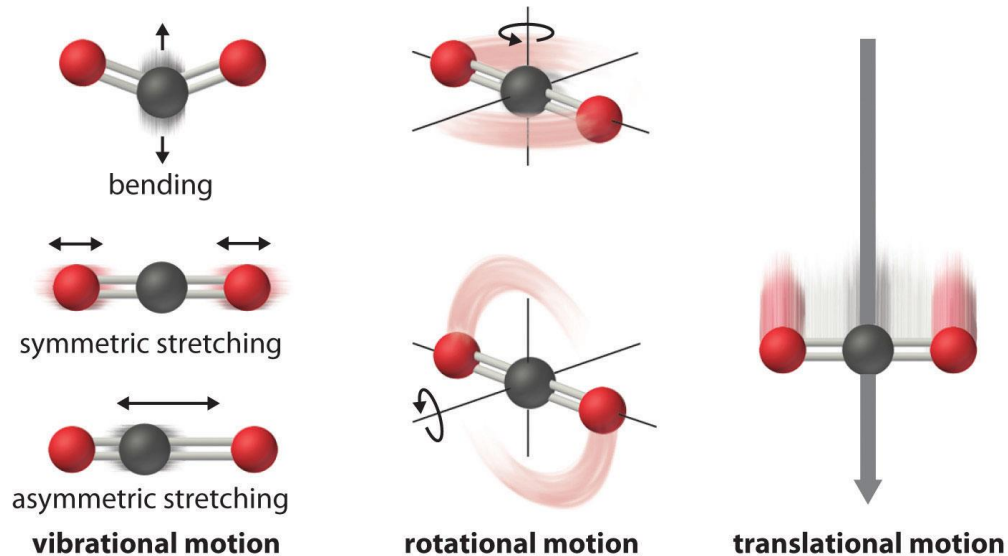
Figure 1: Molecular motions of CO_2 molecule

The third law of thermodynamics has two important consequences:

❖ It defines the *sign* of the entropy of any substance at temperatures above absolute zero as positive.

❖ And it provides a fixed reference point that allows us to measure the *absolute entropy* of any substance at any temperature.

In practice, chemists determine the absolute entropy of a substance by measuring the molar heat capacity (C_p) as a function of temperature and then plotting the quantity C_p/T versus T.

The *area* under the curve between 0 K and any temperature T is the absolute entropy of the substance at T. In contrast, other thermodynamic properties, such as internal energy and enthalpy, can be evaluated in only *relative* terms, not absolute terms.

In this lecture , we examine two different ways to calculate ΔS for a reaction or a physical change:

1- Calculating ΔS from Standard Molar Entropy Values

One way of calculating ΔS for a reaction is to use tabulated values of the **_standard molar entropy ($S^\bullet$),_** _which is the entropy of 1 mol of a substance at a standard temperature of 298 K; the units of $S°$ are J/(mol·K)._

Unlike enthalpy or internal energy, it is possible to obtain absolute entropy values by measuring the entropy change that occurs between the reference point of 0 K [corresponding to $S = 0$ J/(mol·K)] and 298 K.

As shown in Table 1 "Standard Molar Entropy Values of Selected substances at 25°C",

- For substances with approximately the same molar mass and number of atoms, $S°$ values fall in the order $S°(gas) > S°(liquid) > S°(solid)$. For instance, $S°$ for liquid water is 70.0 J/(mol·K), whereas $S°$ for water vapor is 188.8 J/(mol·K). Likewise, $S°$ is 260.7 J/(mol·K) for gaseous I_2 and 116.1 J/(mol·K) for solid I_2. This order makes qualitative sense based on the kinds and extents of motion available to atoms and molecules in the three phases.
- also reveals that substances with similar molecular structures tend to have similar $S°$ values.
- Among crystalline materials, those with the lowest entropies tend to be rigid crystals composed of small atoms linked by strong, highly directional bonds, such as diamond [$S° = 2.4$ J/(mol·K)]. In contrast, graphite, the softer, less rigid allotrope of carbon, has a higher $S°$ [5.7 J/(mol·K)] due to more disorder in the crystal.
- the absolute entropy of a substance tends to increase with increasing molecular complexity because the number of available microstates increases with molecular complexity. For example, compare the $S°$ values for $CH_3OH(l)$ and $CH_3CH_2OH(l)$.
- Finally, substances with strong hydrogen bonds have lower values of $S°$, which reflects a more ordered structure.

Table 1: Standard Molar Entropy Values of Selected Substances at 25°C

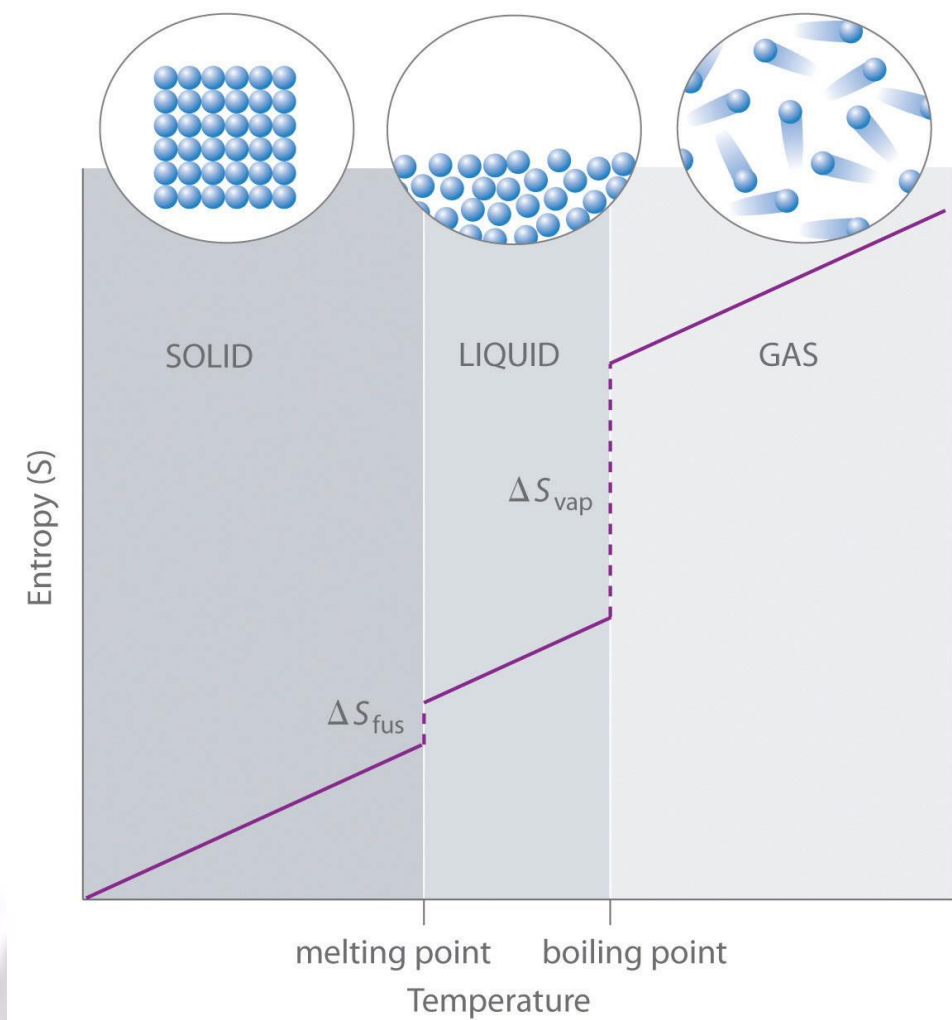| Substance	$S°$ [J/(mol·K)]
Gases	
He	126.2
H_2	130.7
Ne	146.3
Ar	154.8
Kr	164.1
Xe	169.7
H_2O	188.8
N_2	191.6
O_2	205.2
CO_2	213.8
I_2	260.7
Liquids	
H_2O	70.0
CH_3OH	126.8
Br_2	152.2
CH_3CH_2OH	160.7
C_6H_6	173.4
CH_3COCl	200.8
C_6H_{12} (cyclohexane)	204.4
C_8H_{18} (isooctane)	329.3
Solids	
C (diamond)	2.4
C (graphite)	5.7
LiF	35.7
SiO_2 (quartz)	41.5
Ca	41.6
Na	51.3
MgF_2	57.2
K	64.7
NaCl	72.1
KCl	82.6
I_2	116.1

Figure 2: A Generalized Plot of Entropy versus Temperature for a Single Substance

To calculate $\Delta S°$ for a chemical reaction from standard molar entropies, we use the familiar "products minus reactants" rule, in which the absolute entropy of each reactant and product is multiplied by its stoichiometric coefficient in the balanced chemical equation.

7 illustrates this procedure for the combustion of the liquid hydrocarbon isooctane (C_8H_{18}; 2,2,4-trimethylpentane).

Example 7

Use the data in Table 1 "Standard Molar Entropy Values of Selected Substances at 25°C" to calculate $\Delta S°$ for the reaction of liquid isooctane with $O_2(g)$ to give $CO_2(g)$ and $H_2O(g)$ at 298 K.

Solution:

The balanced chemical equation for the complete combustion of isooctane (C_8H_{18}) is as follows:

$$C_8H_{18}(l)+ \frac{25}{2}O2(g) \rightarrow 8CO_2(g)+9H_2O(g)$$
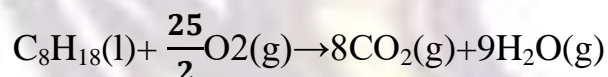
We calculate $\Delta S°$ for the reaction *using the "products minus reactants" rule,* where m and n are the stoichiometric coefficients of each product and each reactant:

$\Delta S°rxn=\sum mS°(\text{products})-\sum nS°(\text{reactants})$

$$=[8S°(CO_2)+9S°(H_2O)]-[S°(C_8H_{18})+ \frac{25}{2}S°(O2)]$$

$$=\{[8 \text{ mol } CO_2 \times 213.8 \text{ J/(mol·K)}]+[9 \text{ mol } H_2O \times 188.8 \text{ J/(mol·K)}]\}$$
$$-\{[1 \text{mol } C_8H_{18} \times 329.3 \text{ J/(mol·K)}]+[\frac{25}{2} \text{mol } O_2 \times 205.2 \text{ J/(mol·K)}]\}$$

$$=515.3 \text{ J/K}$$

$\Delta S°$ is positive, as expected for a combustion reaction in which one large hydrocarbon molecule is converted to many molecules of gaseous products.

Homework :Use the data in Table 18.1 "Standard Molar Entropy Values of Selected Substances at 25°C" to calculate $\Delta S°$ for the reaction of $H_2(g)$ with liquid benzene (C_6H_6) to give cyclohexane (C_6H_{12}).

Answer: −361.1 J/K

2- Calculating ΔS from Thermodynamic Cycles

We can also calculate a change in entropy using a thermodynamic cycle.

The molar heat capacity

(C_p) :is the amount of heat needed to raise the temperature of 1 mol of a substance by 1°C at constant pressure.

(C_v) is the amount of heat needed to raise the temperature of 1 mol of a substance by 1°C at constant volume.

the change in entropy for a substance whose temperature changes from T_1 to T_2 is as follows:

$$\Delta S = q_{rev} / T = nC_p \, \Delta T / T \quad \text{(constant pressure}$$

$$\Delta S = n \, C_p \ln T2 / T1 \quad \text{(constant pressure)}.........(1)$$

$$\Delta S = nC_v \ln T2 / T1 \quad \text{(constant volume)}...........(2)$$

$$\Delta S_{fus} = \frac{q_{rev}}{T} = \frac{\Delta H_{fus}}{T}.......................(3)$$

Thus we can use a combination of heat capacity measurements (Equation 1 or Equation 2) and experimentally measured values of enthalpies of fusion or vaporization if a phase change is involved (Equation 3) to calculate the entropy change corresponding to a change in the temperature of a sample.
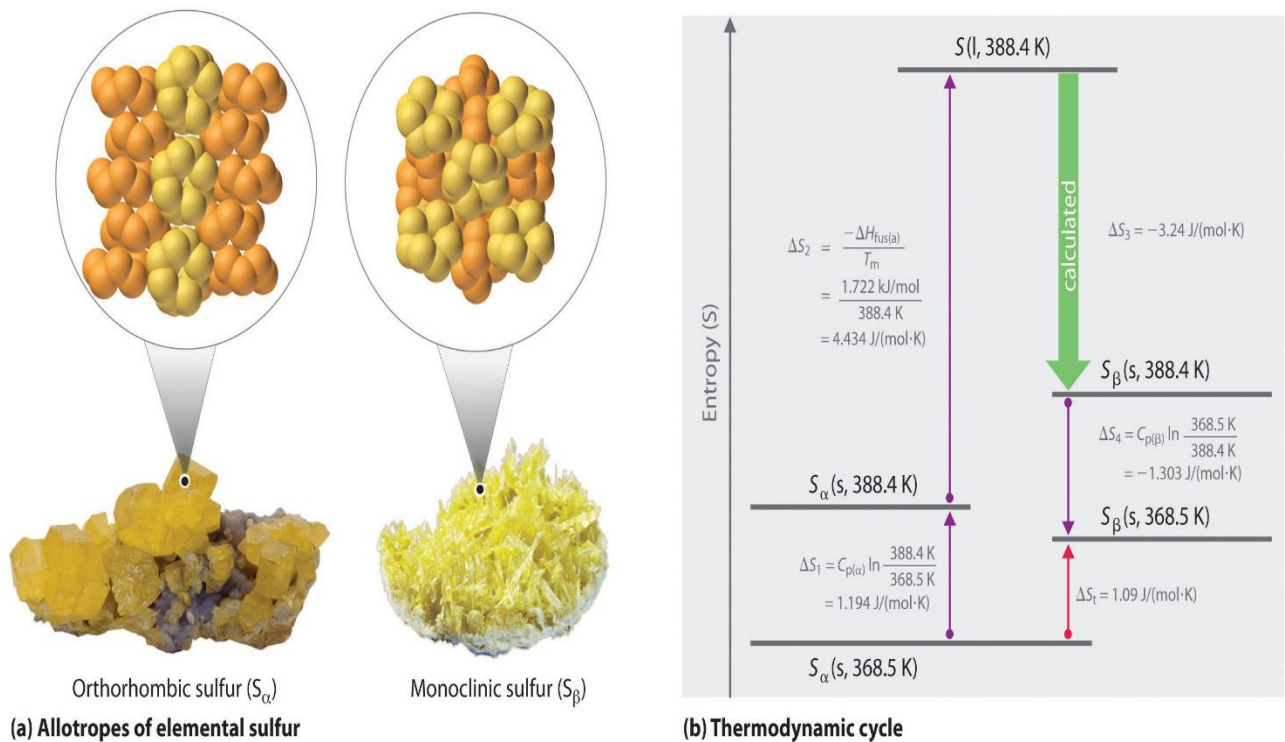
Figure 3: Two Forms of Elemental Sulfur and a Thermodynamic Cycle Showing the Transition from One to the Other:

We can use a thermodynamic cycle to calculate the entropy change when the phase change for a substance such as sulfur cannot be measured directly.

elemental sulfur exists in two:

1-An orthorhombic form with a highly ordered structure (S_α)

2- a less-ordered monoclinic form (S_β).

The orthorhombic (α) form is more stable at room temperature but undergoes a phase transition to the monoclinic (β) form at temperatures greater than 95.3°C (368.5 K). The transition from S_α to S_β can be described by the thermodynamic cycle shown in part (b) in Figure 3, in which liquid sulfur is an intermediate. The change in entropy that accompanies the conversion of liquid sulfur to S_β ($-\Delta S_{fus(\beta)} = \Delta S_3$ in the cycle) cannot be measured directly. Because entropy is a state function, however, ΔS_3 can be calculated from the

overall entropy change (ΔS_t) for the S_α–S_β transition, which equals the sum of the ΔS values for the steps in the thermodynamic cycle, using Equation 18.20 and tabulated thermodynamic parameters (the heat capacities of S_α and S_β, $\Delta H_{fus(\alpha)}$, and the melting point of S_α.)

(a) Orthorhombic sulfur (S_α) has a highly ordered structure in which the S_8 rings are stacked in a "crankshaft" arrangement. Monoclinic sulfur (S_β) is also composed of S_8 rings but has a less-ordered structure.

(b) At 368.5 K, S_α undergoes a phase transition to S_β. Although ΔS_3 cannot be measured directly, it can be calculated using the values shown in this thermodynamic cycle.

If we know the melting point of S_α (T_m = 115.2°C = 388.4 K) and ΔS_t for the overall phase transition [calculated to be 1.09 J/(mol·K) in the exercise in Example 6], we can calculate ΔS_3 from the values given in part (b) in Figure 18.15 "Two Forms of Elemental Sulfur and a Thermodynamic Cycle Showing the Transition from One to the Other" where $C_{p(\alpha)}$ = 22.70 J/mol·K and $C_{p(\beta)}$ = 24.77 J/mol·K (subscripts on ΔS refer to steps in the cycle):

ΔS_t 1.09 J/(mol·K) = $\Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4$

$= C_p(\alpha)\ln\left(\dfrac{T_2}{T_1}\right) + \dfrac{\Delta H_{fus}}{T_m} + \Delta S_3 + C_p(\beta)\ln\left(\dfrac{T_4}{T_3}\right) = 22.70 \text{ J/(mol·K)}\ln\left(\dfrac{388.4}{368.5}\right) + \left(\dfrac{1.722 \text{ kJ/mol}}{388.4 \text{ K}} \times 1000 \text{ J/kJ}\right) + \Delta S_3 + 24.77 \text{ J/(mol·K)}\ln\left(\dfrac{368.5}{388.4}\right)$

$= [1.194 \text{ J/(mol·K)}] + [4.434 \text{ J/(mol·K)}] + \Delta S_3 + [-1.303 \text{ J/(mol·K)}]$

Solving for ΔS_3 gives a value of −3.24 J/(mol·K). As expected for the conversion of a less ordered state (a liquid) to a more ordered one (a crystal), ΔS_3 is negative.

Summary

- The **third law of thermodynamics** states that the entropy of any perfectly ordered, crystalline substance at absolute zero is zero.
- At temperatures greater than absolute zero, entropy has a positive value, which allows us to measure the *absolute entropy* of a substance.
- Measurements of the heat capacity of a substance and the enthalpies of fusion or vaporization can be used to calculate the changes in entropy that accompany a physical change.
- The entropy of 1 mol of a substance at a standard temperature of 298 K is its **standard molar entropy** ($S°$).
- We can use the "products minus reactants" rule to calculate the standard entropy change ($\Delta S°$) for a reaction using tabulated values of $S°$ for the reactants and the products.

The Carnot Cycle

The Carnot cycle consists of the following four processes:

I. A reversible isothermal gas expansion process. In this process, the ideal gas in the system absorbs q_{in} amount heat from a heat source at a high temperature Th, expands and does work on surroundings.

II. A reversible adiabatic gas expansion process. In this process, the system is thermally insulated. The gas continues to expand and do work on surroundings, which causes the system to cool to a lower temperature, Tl.

III. A reversible isothermal gas compression process. In this process, surroundings do work to the gas at Tl, and causes a loss of heat, q_{out}.

III. A reversible adiabatic gas compression process. In this process, the system is thermally insulated. Surroundings continue to do work to the gas, which causes the temperature to rise back to Th.
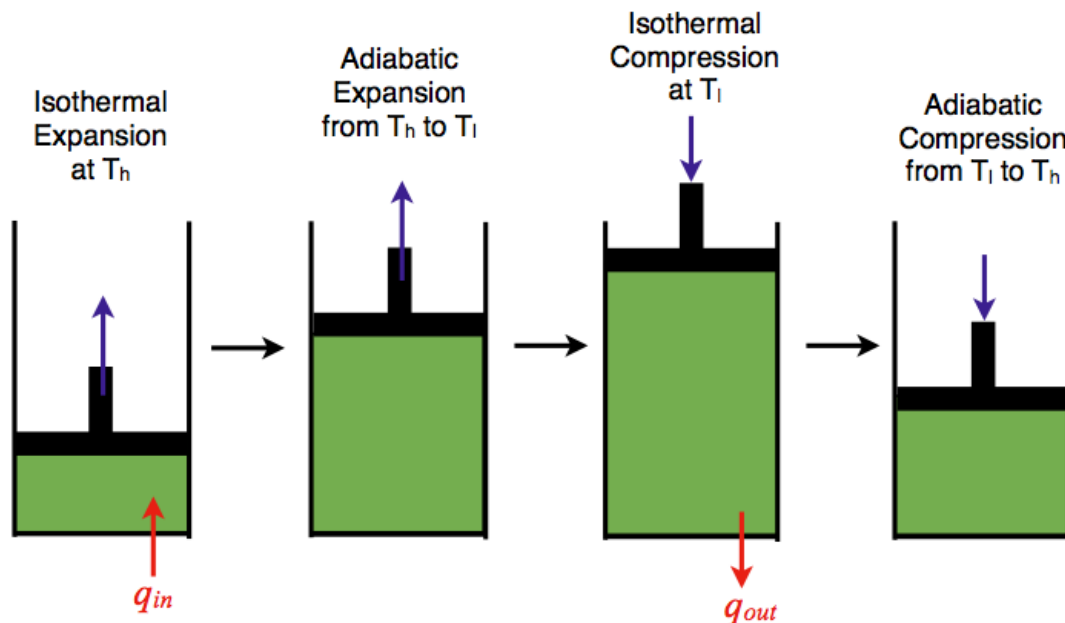

Figure 1: An ideal gas-piston model of the Carnot cycle.

P-V Diagram

The P-V diagram of the Carnot cycle is shown in Figure 2. In isothermal processes I and III, $\Delta U=0$ because $\Delta T=0$. In adiabatic processes II and IV, $q=0$. Work, heat, ΔU, and ΔH of each process in the Carnot cycle are summarized in Table 1.
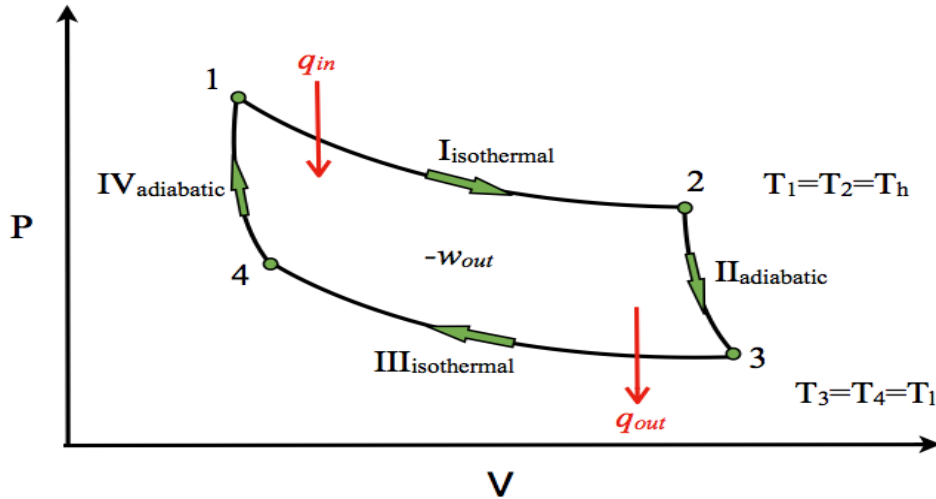

Figure 2: A P-V diagram of the Carnot Cycle.

Process	w	q	ΔU	ΔH
I	$-nRT_h \ln\left(\dfrac{V_2}{V_1}\right)$	$nRT_h \ln\left(\dfrac{V_2}{V_1}\right)$	0	0
II	$n\bar{C}_v(T_l - T_h)$	0	$n\bar{C}_v(T_l - T_h)$	$n\bar{C}_p(T_l - T_h)$
III	$-nRT_l \ln\left(\dfrac{V_4}{V_3}\right)$	$nRT_l \ln\left(\dfrac{V_4}{V_3}\right)$	0	0
IV	$n\bar{C}_v(T_h - T_l)$	0	$n\bar{C}_v(T_h - T_l)$	$n\bar{C}_p(T_h - T_l)$
Full Cycle	$-nRT_h \ln\left(\dfrac{V_2}{V_1}\right) - nRT_l \ln\left(\dfrac{V_4}{V_3}\right)$	$nRT_h \ln\left(\dfrac{V_2}{V_1}\right) + nRT_l \ln\left(\dfrac{V_4}{V_3}\right)$	0	0

Table 1. Work, heat, ΔU, and ΔH in the P-V diagram of the Carnot Cycle

T-S Diagram

The T-S diagram of the Carnot cycle is shown in Figure 3. In isothermal processes I and III, ΔT=0. In adiabatic processes II and IV, ΔS=0 because dq=0. ΔT and ΔS of each process in the Carnot cycle are shown in Table 2.

Figure 3: A T-S diagram of the Carnot Cycle.
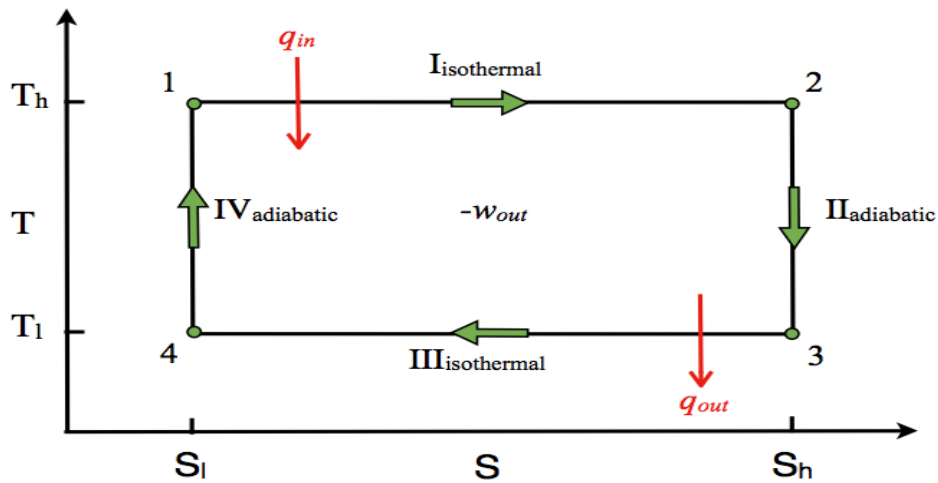
Process	ΔT	ΔS
I	0	$-nRln\left(\dfrac{V_2}{V_1}\right)$
II	$T_l - T_h$	0
III	0	$-nRln\left(\dfrac{V_4}{V_3}\right)$
IV	$T_h - T_l$	0
Full Cycle	0	0

Table 2. ΔT and ΔS in the T-S diagram of the Carnot Cycle

Efficiency

The Carnot cycle is the most efficient engine possible based on the assumption of the absence of incidental wasteful processes such as friction, and the assumption of no conduction of heat between different parts of the engine at different temperatures. The

efficiency of the Carnot engine is defined as the ratio of the energy output to the energy input.

$$\text{efficiency} = \frac{\text{net work done by heat engine}}{\text{heat absorbed by heat engine}} = \frac{-w_{sys}}{q_h} \tag{1.1}$$

$$= \frac{nRT_h \ln\left(\frac{V_2}{V_1}\right) + nRT_l \ln\left(\frac{V_4}{V_3}\right)}{nRT_h \ln\left(\frac{V_2}{V_1}\right)} \tag{1.2}$$

$$\left(\frac{T_2}{T_3}\right)^{C_V/R} = \frac{V_3}{V_2} \tag{1.3}$$

$$\left(\frac{T_1}{T_4}\right)^{C_V/R} = \frac{V_4}{V_1} \tag{1.4}$$

$$\frac{V_3}{V_4} = \frac{V_2}{V_1} \tag{1.5}$$

$$\text{efficiency} = \frac{nRT_h \ln\left(\frac{V_2}{V_1}\right) - nRT_l \ln\left(\frac{V_2}{V_1}\right)}{nRT_h \ln\left(\frac{V_2}{V_1}\right)} \tag{1.6}$$

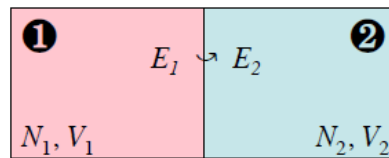$$\boxed{\text{efficiency} = \frac{T_h - T_l}{T_h}} \tag{1.7}$$

Chemical potential…

Thermal equilibrium

Energy exchange between 1 and 2

$$E_1 + E_2 = E^{tot} \Rightarrow dE_2 = -dE_1$$

At equilibrium, entropy S is maximum

$$dS = dS_1 + dS_2 \quad = \frac{\partial S_1}{\partial E_1} dE_1 + \frac{\partial S_2}{\partial E_2} dE_2$$

$$= \frac{\partial S_1}{\partial E_1} dE_1 - \frac{\partial S_2}{\partial E_2} dE_1$$

$$\Longrightarrow \qquad dS = \left(\frac{1}{T_1} - \frac{1}{T_2} \right) dE_1 \geq 0$$

If $T_1 > T_2$ then $1/T_1 - 1/T_2 < 0$ so that $dE_1 \leq 0$

Energy tends to flow from a system with a high value of T to a system with a low value of T. This energy transfer continues until $T_1 = T_2$

Physical meaning of temperature = tendency of a system to give energy

Chemical potential of a proton (H^+) : pH

$$pH = \left(\mu^0_{H+} - \mu_{H+}\right) / RT \ln 10$$

pH : tendency of a solution to take H^+

Chemical potential of water moleculaes : humidity

$$\ln P_{water} / P^0 = \left(\mu_{water} - \mu^0_{water}\right) / RT$$

humidity : tendency of an atmosphere to give water molecules – further units exists following the context (hydric potential, etc…)

Chemical potential of electrons : Nernst potential

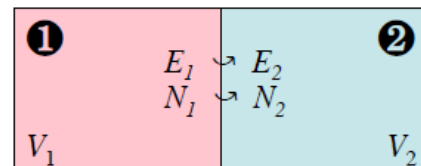$$E = E^0 + \left(\frac{RT}{nF}\right) \ln \frac{a_{Ox}}{a_{Red}} = -\frac{\mu_{e-}}{F} + Cte$$

E : tendency of system to take electrons

Further exemples : pC, pOH, etc…

Chemical equilibrium

Particles exchange between 1 and 2

$$dE_2 = -dE_1 \text{ and } dN_2 = -dN_1$$

At equilibrium, entropy S is maximum

$$dS = dS_1 + dS_2 = \left(\frac{\partial S_1}{\partial E_1} - \frac{\partial S_2}{\partial E_2}\right) dE_1$$

$$+ \left(\frac{\partial S_1}{\partial N_1} - \frac{\partial S_2}{\partial N_2}\right) dN_1$$

$$\Longrightarrow \quad dS = \left(-\frac{\mu_1}{T_1} + \frac{\mu_2}{T_2}\right) dV_1 \geq 0 \quad (\text{if } T_1 = T_2 = T$$

If $\mu_1 > \mu_2$, $dN_1 \leq 0$

Particles tends to flow from a system with a high value of μ to a system with a high value of μ. This particle transfer continues until $\mu_1 = \mu_2$

> Physical meaning of chemical potential
> = tendency of a system to give particles
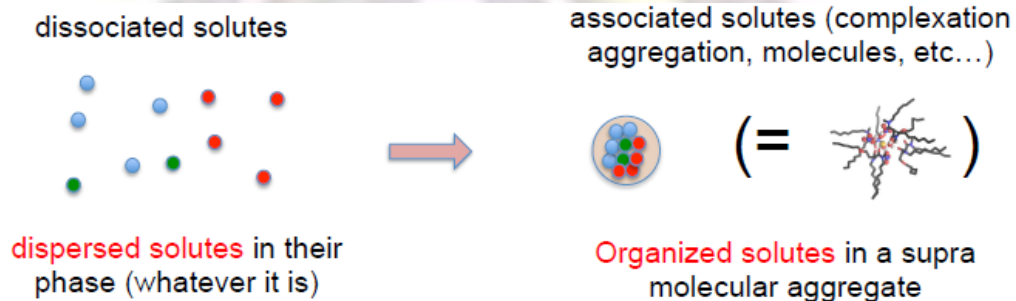
Ideal terms are typically valid

1. For ideal mixtures (perfect gas, etc…)
2. At low concentration (gas, solute particles)
3. At high concentration (solvent, liquid or solid mixtures)

Typically :

- Valid for 1 and 2 because the interactions between the particles are not important
- Valid for 3 because of Gibbs-Duhem relation

Activity coefficients represent the interactions between the particles that are not included in the standard term.

- solute/solute interactions for solutions
  - intermolecular interactions for gas

dissociated solutes

associated solutes (complexation aggregation, molecules, etc…)

dispersed solutes in their phase (whatever it is)

Organized solutes in a supra molecular aggregate

Free energy calculation

c = typical concentration of solutes n = agregation number

$$G^{init} = \sum_i \mu_i^0 + NRT \ln \frac{c}{c^0} \qquad G^{final} = \mu_{agg}^0 + RT \ln \frac{c}{c^0}$$

Difference $\Delta G = (1-N)RT \ln c + Cte$

If the solutes are diluted (small c), ΔG becomes infinitely high.

association becomes not stable – at high dilution entropy always wins

$$\Delta G = (1 - N)RT \ln c + \text{Cte} \qquad \frac{\Delta G}{N} \approx -RT \ln c + \Delta G^0 / N$$

No supramolecular organisation for infinite dilute systems

- Ostwald law (weak acids or electrolytes become strong if dilute)

- critical micellar concentration : micelles do not exist if dilute

- re-extraction from dilution (add solvent for re-extraction)

- no molecules in an infinite space

$$\frac{\Delta G}{N} \approx -RT \ln c + \Delta G^0 / N \qquad \begin{cases} c \geq 10^{24} \Rightarrow \Delta G^0 / N \leq 50 \, k_BT \approx 100 \text{ kJ.mol}^{-1} \\ c \geq 10^{12} \Rightarrow \Delta G^0 / N \leq 25 \, k_BT \approx 50 \text{ kJ.mol}^{-1} \end{cases}$$

weak forces are forces that can be overcome by configurationnal entropy

Standard term

Molar free enthalpy of a particle at the standard state, i.e.

- gas phase : one single molecule (because dilute)

- liquid mixture, solid mixture and solvent : pure system

- solute particles : one single solute particle dispersed in the solvent

☐ relatively easy evaluation (no correlation)

Consequence for the standard chemical potential

$$\mu^0 = \mu_{\text{nucl}}^{\text{int}} + \mu_{\text{nucl}}^{\text{trans}} + \mu_{\text{elect}}$$

$$\mu_{\text{nucl}}^{\text{trans}} = -k_BT \ln\left[\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \frac{k_B T}{P^0}\right]$$

$$\mu_{\text{elec}} = -k_BT \ln\left[\omega_0 + \omega_1 \exp(-\varepsilon_1 / k_B T) + ...\right]$$

↑ ↑ ↑

degeneracy and energy
of the electronic levels

Experimental validation
for the entropy

	exp.	calc.	
He	30.13	30.11	
Ne	34.95	34.94	
Ar	36.98	36.97	e.u.
Kr	39.19	39.18	
Xe	40.53	40.52	
Hg	41.8	41.78	