

# Communication: A Simpler and More Applicable 2<sup>nd</sup> Law of Thermodynamics

Kuo-Chung Liu 

Kaohsiung

Email: kcliu2734@yahoo.com.tw

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## Abstract

The author derived the rule of Atomistic 2<sup>nd</sup> Law of Thermodynamics which is more compatible with Mother Nature, and is simpler and more applicable. A comparison between the Atomistic and Classic 2<sup>nd</sup> Law of Thermodynamics is reported, and the former can be regarded as the widening of the latter. Based on atomistic view, it's apparent that the 1<sup>st</sup> and 2<sup>nd</sup> Laws of Thermodynamics are closely related. The reported examples are: surface energy, osmotic pressure, reverse osmosis, total potential of interface, chemical potential of gas phase, chemical reaction in gases, chemical reaction in condensed phases, surface tension of liquid, capillary, and thermocouple. The discussed topics are: kinetics should come first, catalyst and activation energy, why the atmosphere of Earth does not diffuse to outer space? Atmosphere of Venus or Mercury, chemical potential and temperature, redox reactions, merging between small and large liquid drops, other driving forces, and non-applicability of the Atomistic 2<sup>nd</sup> Law of Thermodynamics.

## Keywords

Atomistic Features, Chemical Potential, Interaction, Spontaneous Evolution, Driving Force, Surface Energy, Interface, Surface Tension, Osmotic Pressure, Reverse Osmosis, Concentration, Capillary, Thermocouple, Kinetics, Phase Transition, Diffusion, Redox, Mergence

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## 1. Introduction

The Classic 2<sup>nd</sup> Law of Thermodynamics is taught to every student of engineering and natural sciences. It is a powerful tool in engineering problems when temperatures and pressures are controllable. But in daily life or work, how many of us can apply the Classic 2<sup>nd</sup> Law of Thermodynamics to spontaneous evolutions? No-

table examples include surface and interface phenomena, surface tension, osmotic pressure, reverse osmosis, capillary, thermocouple, etc.

The Classic 2<sup>nd</sup> Law of Thermodynamics is macroscopic in nature. However, when a system spontaneously evolves to a more stable state, it is through the movements of atomistic features like atoms, molecules, ions, etc. Therefore, logical questions arise, including:

(1) How would these atomistic features know “to where they should move?”

(2) How would these atomistic features know “their movements would result in the Classic 2<sup>nd</sup> Law of Thermodynamics macroscopically?”

The author deeply believes that the atomistic features can only follow their given nature. As a result, the 2<sup>nd</sup> Law of Thermodynamics should have an atomistic origin. After the author’s study, he finds that the rule of the Atomistic 2<sup>nd</sup> Law of Thermodynamics should be “at equilibrium, the total potential of atomistic features is at minimum”. When the potentials other than chemical potential can be neglected, the total potential is equal to the total chemical potential.

With this perception, the Classic 2<sup>nd</sup> Law of Thermodynamics, developed by many very wise ancestors<sup>1</sup>, becomes the resulting observations of this rule.

Moreover, temperature and pressure are human-made parameters and both are the averages of many atomistic features. It is impossible for Mother Nature to know these parameters. Hence, Mother Nature needs neither temperature nor pressure to describe the 2<sup>nd</sup> Law of Thermodynamics. As reported in the following, the Atomistic 2<sup>nd</sup> Law of Thermodynamics also requires neither temperature nor pressure, therefore is more compatible with Mother Nature (although the chemical potential of atomistic features will depend on temperature or pressure).

## 2. Comparison between Atomistic and Classic 2<sup>nd</sup> Law of Thermodynamics

A comparison between the Atomistic and Classic 2<sup>nd</sup> Law of Thermodynamics can be made for an equilibrium system with one component, where the only important potential is chemical potential. The comparison is shown in **Table 1**:

**Table 1.** A comparison between Classic and Atomistic 2<sup>nd</sup> Law of Thermodynamics for a one component system at equilibrium.

System condition	Classic 2 <sup>nd</sup> Law	Atomistic 2 <sup>nd</sup> Law
Isolated	Entropy $S$ is maximum	Chemical potential $N\mu$ is minimum
Close	Internal energy $E$ is minimum	Chemical potential $N\mu$ is minimum
Close and equal-pressure	Enthalpy $H$ is minimum	Chemical potential $N\mu$ is minimum
Close and isothermal	Helmholtz free energy $F$ is minimum	Chemical potential $N\mu$ is minimum
Close and equal-pressure and isothermal	Gibbs free energy $G$ is minimum	Chemical potential $N\mu$ is minimum

Note:  $N$  is its number of moles,  $\mu$  is its molar chemical potential.

<sup>1</sup>The scholars in 18~19th century, who developed the Classic 2<sup>nd</sup> Law of Thermodynamics, were very wise and had very remarkable achievements, because they developed this very important law only based on experiments and inferences without knowing much about the atomistic features.

The system condition in **Table 1** (the left-most column) is categorized as isolated, close, close and equal-pressure, close and isothermal, close and equal-pressure and isothermal. In Classic 2<sup>nd</sup> Law of Thermodynamics (the middle column), one needs to use different parameters (e.g., S, E, H, F, or G) under different system conditions. While in Atomistic 2<sup>nd</sup> Law of Thermodynamics (the right-most column), the rule for equilibrium always is that “chemical potential  $N\cdot\mu$  is minimum” ( $N\cdot\mu$  is similar to one form of Gibbs free energy)<sup>2</sup>, regardless of system conditions.

In **Table 1**,  $N$  is a constant, therefore “the chemical potential  $N\cdot\mu$  is minimum” will become “the molar chemical potential  $\mu$  is minimum”. Its necessary and sufficient condition is “ $\mu$  is the same in the whole system”. Furthermore, although “the chemical potential  $N\cdot\mu$  is minimum” is in the same form at the right-most column of **Table 1**, but the system condition is different. So the corresponding molar chemical potential  $\mu$  also changes differently.

Since the Atomistic 2<sup>nd</sup> Law of Thermodynamics can be applied to any spontaneous evolution toward equilibrium, whether the system is isolated, closed, equal pressure, isothermal or not, it can be regarded as the widening of the Classic 2<sup>nd</sup> Law of Thermodynamics.

### 3. Atomistic 1<sup>st</sup> and 2<sup>nd</sup> Laws of Thermodynamics

The Atomistic 1<sup>st</sup> and 2<sup>nd</sup> Laws of Thermodynamics can be described as follows:

1<sup>st</sup> Law: Energy conservation (same as the Classic 1<sup>st</sup> Law of Thermodynamics). Some energies of atomistic features can transform to other types of energies, but the sum of total kinetic energy and total potential energy will not change.

2<sup>nd</sup> Law: For spontaneous evolutions toward equilibrium, the driving force is “to lower the total potential of the atomistic features”. As a result, the total potential of the system is the lowest at equilibrium. In other words, the total kinetic energy of atomistic features is the highest (but the former is easier to apply).

When described with an atomistic view, it is apparent that the 1<sup>st</sup> and 2<sup>nd</sup> Law of Thermodynamics are closely related. It is unlike the very vague relation between the Classic 1<sup>st</sup> and 2<sup>nd</sup> Laws of Thermodynamics, especially when entropy  $S$  is used to describe the 2<sup>nd</sup> Law of Thermodynamics. Since the 1<sup>st</sup> Law of Thermodynamics is very simple and easy to use, it makes sense that the 2<sup>nd</sup> Law of Thermodynamics also has the same characteristics.

The following points are related to the Atomistic 2<sup>nd</sup> Law of Thermodynamics, and should contribute to the understanding of this law:

- (1) The molar total potential of atomistic features (including condensed and gas phases) can be categorized into: ① molar chemical potential: originated from the interactions among atomistic features, ② other molar potentials: originated from the interactions between atomistic features and the environments, e.g. molar gravitational potential, molar electric potential, molar magnetic potential and etc.
- (2) In liquid phase, the interactions among atomistic features are closely related

<sup>2</sup>Wikipedia (2025): Gibbs Free Energy, in Homogeneous systems. [https://en.wikipedia.org/wiki/Gibbs\\_free\\_energy](https://en.wikipedia.org/wiki/Gibbs_free_energy)

to bonding which is expected to be the source of molar chemical potential. Since bonding will result in a negative potential, the molar chemical potential of liquid phase is negative. Due to the fact that the surface molecules of liquid have less complete bonding than the inner molecules, they'd have a higher (less negative) molar chemical potential.

(3) In gas phase, there is no bonding among atomistic features, therefore, their bonding potential is 0<sup>3</sup>. In this case, the interactions among atomistic features should be closely related to gas concentration. Hence, the molar chemical potential of gas phase is likely dominated by its concentration. Detailed descriptions will be provided in 4.5.

(4) When chemical reactions are at equilibrium, the necessary and sufficient condition of the Atomistic 2<sup>nd</sup> Law of Thermodynamics is “the  $\sum N_i \cdot \mu_i$  of reactants is equal to the  $\sum N_j \cdot \mu_j$  of products”. This rule is the same as  $\Delta G = 0$  in Classic 2<sup>nd</sup> Law of Thermodynamics. When the author derives the equilibrium constant  $K_{eq}$  for gases and condensed phases in 4.6 and 4.7, this is one of the conditions used.

(5) When other potentials, e.g., gravitational potential, electric potential, magnetic potential and etc., should be considered together with chemical potentials, the total potential is the sum of all potentials. The rule of Atomistic 2<sup>nd</sup> Law of Thermodynamics now becomes “the total molar potential of atomistic features is at minimum”. Its necessary and sufficient condition is “the total molar potential is the same in the whole system” which is the basis of 4.8, 4.9 and 4.10.

(6) Heat is originated from the moving of atomistic features, therefore, it is a kinetic energy in nature. In dealing with the spontaneous evolutions using Atomistic 2<sup>nd</sup> Law of Thermodynamics, only the total potential is needed. Therefore, heat is irrelevant. Nevertheless, some heat can change the chemical potential of a substance (e.g., boiling water with heat).

## 4. Examples

The spontaneous evolutions toward equilibrium that can apply Atomistic 2<sup>nd</sup> Law of Thermodynamics or its necessary and sufficient condition are numerous, including:

### 4.1. Surface Energy

The gravitational potential is temporarily ignored. Suppose a glass tube with a rubber head is dripping down a water drop and the system is at room temperature and 1 atm. The molar surface energy per unit surface area of this liquid drop  $\gamma$  can be obtained as follows:

Since the bonding of surface molecules is less complete than inner molecules, the inner molecules must have an extra pressure  $\Delta P$  atm to increase bonding potential (similar to a pressed spring) at equilibrium. And the molar chemical po-

<sup>3</sup>When a condensed phase evaporates, its bonding potential increases from a negative value to 0, thus energy is needed in this process.

tential of inner molecules,  $\mu(1 + \Delta P)$ , can be expanded in Taylor Expansion [1] as:

$$\mu(1 + \Delta P) = \mu(1) + \Delta P \cdot \left[ \frac{\partial \mu(1)}{\partial P} \right] + (1/2) \Delta P^2 \cdot \left[ \frac{\partial^2 \mu(1)}{\partial^2 P} \right] + (\text{remainder}) \quad (\text{Eq.1})$$

In (Eq.1),  $\mu(1)$  is the molar chemical potential of water at 1 atm,  $\left[ \frac{\partial \mu(1)}{\partial P} \right] = v(1)$  and  $\left[ \frac{\partial^2 \mu(1)}{\partial^2 P} \right] = \left[ \frac{\partial \mu(1)}{\partial P} \right] = -\beta(1) \cdot v(1)$ , where  $v(1)$  denotes the molar volume of water at 1 atm,  $\beta(1)$  denotes its compressibility<sup>4</sup>. Hence (Eq.1) can be rewritten as:

$$\mu(1 + \Delta P) = \mu(1) + \Delta P \cdot v(1) - (1/2) \Delta P^2 \cdot \beta(1) \cdot v(1) + (\text{remainder}) \quad (\text{Eq.2})$$

In (Eq.2),  $\Delta P$  is far smaller than 1, and the absolute value of  $-\beta(1) \cdot v(1)$  is far smaller than  $v(1)$ . Hence the absolute value of  $-(1/2) \Delta P^2 \cdot \beta(1) \cdot v(1)$  is far smaller than  $\Delta P \cdot v(1)$ . The absolute value of the remainder is even smaller, thus all of them can be neglected. As a result, (Eq. 2) can be approximated as:

$$\mu(1 + \Delta P) \doteq \mu(1) + \Delta P \cdot v(1) \quad (\text{Eq.3})$$

If  $\mu(1)_{\text{surface}}$  denotes the molar chemical potential of surface molecules at 1 atm, then the molar surface energy per unit area at 1 atm,  $\gamma$ , can be defined as:

$$\mu(1)_{\text{surface}} = \mu(1) + \gamma \cdot A \quad (\text{Eq.4})$$

Here A denotes the surface area of this water drop. Since the inner molecules of a water drop are at equilibrium with their surface molecules, we have:

$$\mu(1 + \Delta P) = \mu(1)_{\text{surface}} \quad (\text{Eq.5})$$

From (Eq.3), (Eq.4), and (Eq.5) we can derive:

$$\mu(1) + \Delta P \cdot v(1) \doteq \mu(1) + \gamma \cdot A \quad (\text{Eq.6})$$

$$i.e. \gamma \doteq \left[ \Delta P \cdot v(1) \right] \div A \quad (\text{Eq.7})$$

In (Eq.7),  $v(1)$  is a constant, A is measurable. If the extra pressure  $\Delta P$  atm is known, then  $\gamma$  can be calculated (and vice versa).

It should be noted:

(a) For a small water drop, the bonding of surface molecules is less complete than that of a large liquid drop, hence  $\mu(1 + \Delta P)$  and  $\Delta P$  atm are both higher for a small water drop.

(b) (Eq.7) shows that  $\gamma$  is proportional to the extra pressure  $\Delta P$  atm and is inversely proportional to the surface area A of the water drop. Therefore, the  $\gamma$  of a small water drop is much higher than that of a large one.

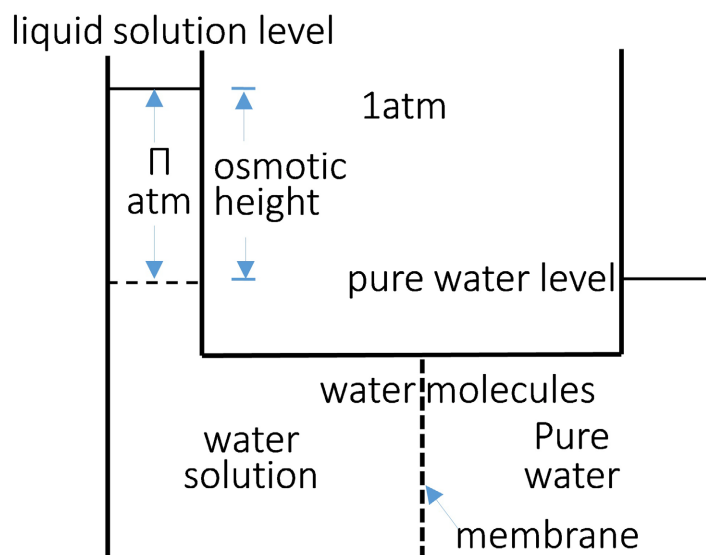
On Earth, since the water molecules of small drop have different height, they will have different gravitational potential. In order to have the same total potential (*i.e.* the sum of chemical potential and gravitational potential) for the molecules

<sup>4</sup>Wikipedia (2024), Compressibility. <https://en.wikipedia.org/wiki/Compressibility>

of the whole water drop, the water drop is not perfectly spherical.

## 4.2. Osmotic Pressure

In **Figure 1**, only the water molecules are small enough to penetrate through the holes of membrane and reach equilibrium on the two sides of membrane. Conversely, the solute molecules in water solution are too large to penetrate through, hence, they cannot reach equilibrium on the two sides of membrane.



**Figure 1.** A system with osmotic pressure  $\Pi$  atm (the holes in membrane are so small that they can only allow pure water molecules to penetrate through).

The figure by Martin Chapman on the chemical potentials of water and water solution [2] shows that the chemical potential of water molecules in water solution is lower than that of pure water. According to the necessary and sufficient condition of Atomistic 2<sup>nd</sup> Law of Thermodynamics, the water molecules in pure water will penetrate through the membrane until the chemical potential of water molecules is equal on the two sides of membrane. At this equilibrium condition, an osmotic pressure  $\Pi$  atm is formed in water solution.

Although A. Grattoni and M. Merlo had reported their findings on osmotic pressure in J. of Physical Chemistry in 2007 [3], the author will present more detailed descriptions based on the necessary and sufficient condition of Atomistic 2<sup>nd</sup> Law of Thermodynamics. In the following derivation, the author would only focus on the height of pure water level at both sides. Hence, only the applied pressure 1 atm and the osmotic pressure  $\Pi$  atm are relevant, and the gravitational potential is not needed.

If the water solution has an osmotic pressure  $\Pi$  atm at 1 atm, WS denotes water solution, then  $\mu(1+\Pi)_{ws}$  is the molar chemical potential of water in water solution at the height of pure water level. The  $\mu(1+\Pi)_{ws}$  can be expanded in Taylor Expansion and approximated in a way similar to (Eq.1) and (Eq.2) as:

$$\mu(1+\Pi)_{ws} = \mu(1)_{ws} + \Pi \cdot \left[ \frac{\partial \mu(1)}{\partial P} \right]_{ws} + (1/2)\Pi^2 \cdot \left[ \frac{\partial^2 \mu(1)}{\partial^2 P} \right]_{ws} + (\text{remainder}) \quad (\text{Eq.8})$$

$$\text{and } \mu(1+\Pi)_{ws} \doteq \mu(1)_{ws} + \Pi \cdot v(1)_{ws} \quad (\text{Eq.9})$$

Where  $v(1)_{ws}$  denotes the molar volume of water solution at 1 atm. Since water molecules in both sides are at equilibrium, *i.e.*  $\mu(1+\Pi)_{ws} = \mu(1)_{\text{pure water}}$ , hence:

$$\mu(1)_{ws} + \Pi \cdot v(1)_{ws} \doteq \mu(1)_{\text{pure water}} \quad (\text{Eq.10})$$

$$\Pi \doteq \left[ \mu(1)_{\text{pure water}} - \mu(1)_{ws} \right] \div v(1)_{ws} \quad (\text{Eq.11})$$

On Earth, 1 atm is equal to the pressure of 1033.6 cm pure water column, therefore, the value of  $\Pi$  can be obtained as follows:

$$\Pi = (h \cdot \rho) \div (1033.6 \cdot 1) \quad (\text{Eq.12})$$

Where  $h$  denotes the osmotic height (in cm),  $\rho$  denotes the density of water solution (in g/cm<sup>3</sup>), and 1 is the density of pure water. When  $h$  and  $\rho$  are measured, the osmotic pressure  $\Pi$  (in atm) can be calculated according to (Eq. 12), and verified with (Eq. 11).

### 4.3. Reverse Osmosis

When an extra pressure  $\Delta P$  atm is applied to water solution and  $\Delta P$  atm >  $\Pi$  atm, then the chemical potential of the water molecules in water solution becomes larger than that of pure water, *i.e.*:

$$\mu(1+\Delta P)_{ws} > \mu(1+\Pi)_{ws} = \mu(1)_{\text{pure water}} \quad (\text{Eq.13})$$

Therefore, the water molecules in water solution will flow through membrane to the pure water side, and a reverse osmosis occurs. The larger the  $\Delta P$  atm, the larger the  $\mu(1+\Delta P)_{ws}$  and the more driving force is for the water molecules in water solution to penetrate through the membrane.

Pure water from reverse osmosis is a popular technology in some countries. Reverse osmosis can also be used in pressurized seawater desalination, or in getting precious pure water in outer space from the urine of astronauts and etc. When the necessary and sufficient condition of Atomistic 2<sup>nd</sup> Law of Thermodynamics is applied, the interpretations of osmotic pressure and reverse osmosis become quite rigorous.

### 4.4. Total Potential of Interface

When two condensed phases meet and they do not dissolve each other, an interface is formed. The interfacial phenomenon is closely related to the Atomistic 2<sup>nd</sup> Law of Thermodynamics in that: the total potential at interface is minimized. There are different types of interfaces and can be described as follows:

(a) At liquid-solid interface

If the molecules at interface will result in a lower total potential, then the liquid will spread as much as possible to enlarge the interface. For example, a small amount of water will spread when dropped on a wooden desk or on a glassy plate.

The wooden desk or glassy plate is called with aqua affinity.

Conversely, if the molecules at interface will result in a higher total potential, then the liquid will shrink as much as possible to reduce the interface. For example, when a small amount of water falls on a clean lotus leaf. The clean lotus leaf is called hydrophobic. For the same reason, mercury will form a droplet on a wooden desk or glassy plate.

Since the water molecules on lotus leaf have different heights and different gravitational potential, they will have different bonding potential. Hence, the water droplet is not perfectly spherical. Similar phenomenon is true for a mercury droplet.

A more complicated example can be found in water strider. Water strider is an insect that can walk on water surface<sup>5</sup>. This phenomenon can also be explained via the Atomistic 2<sup>nd</sup> Law of Thermodynamics as follows:

1) Water striders have hairy legs and bodies. These hairs are hydrophobic, hence a water strider will not become wet due to these hairs.

2) The bulk density of a water strider is smaller than that of water. Consequently, a water strider will remain on water surface to have a lower total gravitational potential in the system. This phenomenon is similar to oil or a lifebuoy capable of floating on water surface.

3) The extra pressure  $\Delta P$  inside water is an added factor to prevent a water strider from entering water. As a result, water striders can easily walk on water surface.

(b) When two liquids meet:

Two liquids will have an interface because their total potential will become higher after mixing. For example, when water and oil meet. Furthermore, the lighter oil will be on top of water to reduce the total gravitational potential. Conversely, water and alcohol will mix completely, because the total potential will decrease after mixing.

(c) Other

“The total potential is lower” is also the working principle of surfactants. For example, various soaps and cleansers for cleaning and various emulsifiers used in food industry. These surfactants can have very good mixing with other substances because of the lower total potential after mixing.

#### 4.5. Chemical Potential of Gas Phase

It is known from the necessary and sufficient condition of the Atomistic 2<sup>nd</sup> Law of Thermodynamics: a liquid will be at equilibrium with its gas phase when they both have the same chemical potential. Evaporation occurs when the chemical potential of liquid,  $\mu_L$ , is higher than that of its gas phase  $\mu_G$ ; while condensation occurs when  $\mu_G$  is higher than  $\mu_L$ .

As mentioned earlier, it is logical to expect the chemical potential of atomistic features being closely related to the interactions among them. For this reason,  $\mu_L$  is likely dominated by bonding. Since gas phase has no bonding,  $\mu_G$  is likely de-

<sup>5</sup>Some reports say that a *water* strider can walk on water surface because of surface tension. But the author believes the explanations of this communication are more complete.

terminated by concentration. The major constraints are (when other potentials can be neglected):

(a) The gas phase chemical potential must be negative so that it can equal the chemical potential of its liquid phase when they are at equilibrium.

(b) The gas phase chemical potential must be in a form so that the equilibrium constant  $K_{eq}$  of the chemical reaction in gas phases  $aA + bB \leftrightarrow cC + dD$  can be expressed as “ $K_{eq} = ([C]^c \cdot [D]^d) \div ([A]^a \cdot [B]^b)$ ” (which is well accepted).

After trials, the author believes the molar chemical potential  $\mu_G$  of gas molecules can be expressed as:

$$\mu_G = K_0 \cdot \ln(K_{1G} \cdot [G]) \quad (\text{Eq.14})$$

In (Eq.14), besides G denotes gas phase, the explanations of other parameters are as follows:

(a)  $K_0$  is a positive constant common for all substances (*i.e.*, independent of substances), dependent on temperature and pressure, having the same unit as  $\mu_G$ . While  $K_{1G}$  is dependent on materials, temperature and pressure; and  $\ln$  is the natural logarithm.

(b)  $[G]$  denotes the concentration of gas G;  $K_{1G} \cdot [G]$  is without unit, and  $0 \leq K_{1G} \cdot [G] < 1$ . Hence  $\mu_G$  and  $\ln(K_{1G} \cdot [G])$  are both negative (so is  $\mu_i$ ). In addition, the higher is  $[G]$ , the stronger is the interaction among atomistic features, and the larger is  $\mu_G$  (less negative).

The gas concentration in a vacuum chamber is 0, (Eq.14) shows its  $\mu_G$  is  $\sim -\infty$ . The air at Earth surface is with certain concentration, (Eq.14) shows its  $\mu_G$  is much larger than  $\sim -\infty$ . From the necessary and sufficient condition of the Atomistic 2<sup>nd</sup> Law of Thermodynamics, the air at Earth surface will diffuse spontaneously to a vacuum chamber.

#### 4.6. Chemical Reaction in Gases

If all potentials other than chemical potentials can be ignored, and 4 gases A, B, C, D are at equilibrium for the chemical reaction  $aA + bB \leftrightarrow cC + dD$  (a, b, c, d, denote the moles of A, B, C, D respectively), then the necessary and sufficient condition in the Atomistic 2<sup>nd</sup> Law of Thermodynamics is that  $\sum N_i \cdot \mu_i$  of reactants equals  $\sum N_j \cdot \mu_j$  of products. That is:

$$a \cdot \mu_A + b \cdot \mu_B = c \cdot \mu_C + d \cdot \mu_D \quad (\text{Eq.15})$$

When (Eq.14) is applied to A, B, C, D gases, we'll have:

$$\begin{aligned} \mu_A &= k_0 \cdot \ln(k_{1A} \cdot [A]), \quad \mu_B = k_0 \cdot \ln(k_{1B} \cdot [B]) \\ \mu_C &= k_0 \cdot \ln(k_{1C} \cdot [C]), \quad \mu_D = k_0 \cdot \ln(k_{1D} \cdot [D]) \end{aligned} \quad (\text{Eq.16})$$

When this chemical reaction is at equilibrium, the temperature and pressure are the same for gases A, B, C, D. So  $k_0$  is the same for these 4 gases. Plug (Eq.16) into (Eq.15) and eliminate the common factor  $k_0$ , we can derive:

$$a \cdot \{\ln(k_{1A} \cdot [A])\} + b \cdot \{\ln(k_{1B} \cdot [B])\} = c \cdot \{\ln(k_{1C} \cdot [C])\} + d \cdot \{\ln(k_{1D} \cdot [D])\} \quad (\text{Eq.17})$$

Taking a, b, c, d into ln, (Eq.17) becomes:

$$\ln(k_{1A} \cdot [A])^a + \ln(k_{1B} \cdot [B])^b = \ln(k_{1C} \cdot [C])^c + \ln(k_{1D} \cdot [D])^d \quad (\text{Eq.18})$$

Now taking both sides of (Eq.18) as the exponent of mathematical constant  $e$ , it becomes:

$$(k_{1A} \cdot [A])^a \cdot (k_{1B} \cdot [B])^b = (k_{1C} \cdot [C])^c \cdot (k_{1D} \cdot [D])^d \quad (\text{Eq.19})$$

Taking the terms with  $k_i$  to the left side, and the terms with  $[G]$  to the right side, (Eq.19) becomes:

$$(k_{1A}^a \cdot k_{1B}^b) \div (k_{1C}^c \cdot k_{1D}^d) = ([C]^c \cdot [D]^d) \div ([A]^a \cdot [B]^b) \quad (\text{Eq.20})$$

If

$$K_{eq} = (k_{1A}^a \cdot k_{1B}^b) \div (k_{1C}^c \cdot k_{1D}^d) \quad (\text{Eq.21})$$

Then (Eq.20) becomes:

$$K_{eq} = ([C]^c \cdot [D]^d) \div ([A]^a \cdot [B]^b) \quad (\text{Eq.22})$$

(Eq.22) shows the mathematical form of equilibrium constant  $K_{eq}$  for the chemical reaction  $aA + bB \leftrightarrow cC + dD$ . The  $K_{eq}$  obtained is with the same form as conventional methods or that obtained from experiments [4]. But the method used by the author is much simpler and more understandable. In fact, the author only used the following 2 conditions:

(a) The chemical potential of a gas G can be expressed as  $\mu_G = k_0 \cdot \ln(k_{1G} \cdot [G])$  (i.e. Eq.14).

(b) At equilibrium, the  $\sum N_i \cdot \mu_i$  of reactants equals the  $\sum N_j \cdot \mu_j$  of products.

#### 4.7. Chemical Reaction of Condensed Phases

If the chemical reaction of condensed phases A, B, C, D can be expressed as  $aA + bB \leftrightarrow cC + dD$ . The parameters a, b, c, d again are the moles of A, B, C, D respectively. At equilibrium the  $\sum N_i \cdot \mu_i$  of the reactants will equal the  $\sum N_j \cdot \mu_j$  of the products, hence:

$$a \cdot \mu_{A(c)} + b \cdot \mu_{B(c)} = c \cdot \mu_{C(c)} + d \cdot \mu_{D(c)} \quad (\text{Eq.23})$$

In (Eq.23), (c) denotes the condensed phase. Since the condensed phases A, B, C, D are at equilibrium with their own gas phases, the following 4 equations are valid, that is:

$$a \cdot \mu_{A(c)} = a \cdot \mu_{A(g)}, b \cdot \mu_{B(c)} = b \cdot \mu_{B(g)}, c \cdot \mu_{C(c)} = c \cdot \mu_{C(g)}, d \cdot \mu_{D(c)} = d \cdot \mu_{D(g)}$$

(Eq.24) In (Eq.24), (g) denotes the gas phase. Plug (Eq.24) into (Eq.23), we still can get  $a \cdot \mu_{A(g)} + b \cdot \mu_{B(g)} = c \cdot \mu_{C(g)} + d \cdot \mu_{D(g)}$ . Hence  $K_{eq}$  is in the same form as (Eq.22). When  $\mu_{A(g)}$ ,  $\mu_{B(g)}$ ,  $\mu_{C(g)}$ ,  $\mu_{D(g)}$  are obtained through (Eq.22),  $\mu_{A(c)}$ ,  $\mu_{B(c)}$ ,  $\mu_{C(c)}$ ,  $\mu_{D(c)}$  can be obtained through (Eq.24). But now the reac-

tants and products are extended to condensed phases.

It is worth mentioning that:

(a) From (Eq.21), it is known that the equilibrium constant  $K_{eq}$  is dependent on  $k_{1A}$ ,  $k_{1B}$ ,  $k_{1C}$ ,  $k_{1D}$  and  $a$ ,  $b$ ,  $c$ ,  $d$ . Hence, it is feasible to evaluate  $K_{eq}$  from these numbers.

(b) It is also known from Le Chatelier principle [5] that  $K_{eq}$  is dependent on temperature, heat-releasing or heat-absorbing, and other factors.

(c) Chemical reaction  $aA + bB \leftrightarrow cC + dD$  does not necessarily occur at some temperature and pressure. Its prerequisites include: ① it is feasible to have  $c \cdot \mu_C + d \cdot \mu_D$  equals  $a \cdot \mu_A + b \cdot \mu_B$ , ② there is no kinetic constraint in the system (as will be discussed in 5.1).

(d) The prerequisites mentioned are also applicable to other chemical reactions, thermo-disintegrations or a phase transitions. For example, the thermo-disintegration of limestone ( $\text{CaCO}_3$ ) into  $\text{CaO}$  and  $\text{CO}_2$  only occurs at high temperature, and the transformation of carbon or graphite into diamond only occurs at very high temperatures and very high pressures [6].

#### 4.8. Surface Tension of Liquid

When a liquid drop falls on a solid, a liquid-gas-solid contact line is formed. The characteristics of the liquid molecules on this contact line are:

- (a) Having a bonding with gas phase;
- (b) Having a bonding with solid;
- (c) Having far less liquid bonding compared to other liquid molecules on surface.

The total molar potential that should be considered is the molar chemical potential and molar gravitational potential. It can be inferred based on the necessary and sufficient condition of the Atomistic 2<sup>nd</sup> Law of Thermodynamics that: the movable liquid at this contact line will adjust its curvature and bonding so that all liquid molecules on surface have the same total molar potential. Due to the curvature on the liquid surface, we normally say that this curvature arises from the surface tension of liquid.

#### 4.9. Capillary

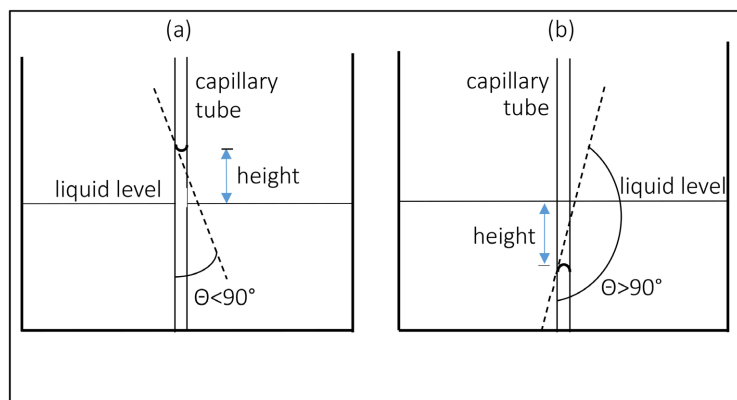


Figure 2. (a)  $\Theta < 90^\circ$ , (b)  $\Theta > 90^\circ$ .

When a capillary tube is inserted into a liquid, the liquid inside the capillary tube will form a meniscus on surface. The angle  $\Theta$  of this meniscus can be smaller than  $90^\circ$  (meniscus is concave) or larger than  $90^\circ$  (meniscus is convex), as shown in **Figure 2(a)** and **Figure 2(b)**.

The necessary and sufficient condition of the Atomistic 2<sup>nd</sup> Law of Thermodynamic for capillary is: “the total molar potential of the liquid molecules is the same everywhere”. In this case, the total molar potential is the sum of the molar chemical potential and the molar gravitational potential. For the liquid inside this capillary, the analysis is as follows:

(a)  $\Theta < 90^\circ$

When the capillary wall and the liquid form an angle  $\Theta < 90^\circ$ , the bonding potential at the interface is lower than other liquid molecules. As a result:

1) This meniscus will rise until its liquid molecules have a higher gravitational potential that can compensate their lower bonding potential with the capillary wall;

2) In this case, the meniscus is concave so that its surface molecules have more bonding and lower bonding potential compared to a flat surface;

3) Among the surface molecules at the meniscus, the lower ones will have lower gravitational potentials and higher bonding potentials. Therefore, the meniscus is not perfectly spherical.

The smaller diameter is the capillary tube, the larger is the bonding ratio between the liquid molecules and the capillary wall. Hence, the meniscus will rise higher and the capillary effect is more pronounced. On Earth, capillary phenomenon is the reason why plants can send water along their trunk to the top of plants (against gravity).

(b)  $\Theta > 90^\circ$

The case of  $\Theta > 90^\circ$  is similar to the case  $\Theta < 90^\circ$ . The major differences are:

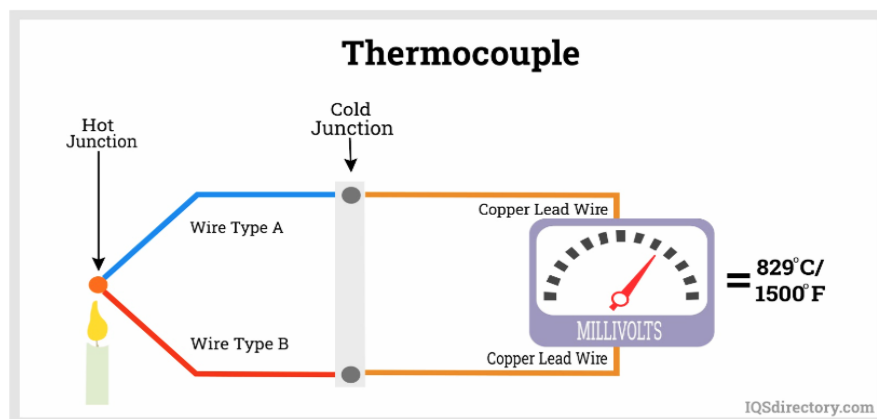
1) The bonding between the liquid molecules and the capillary wall now has a higher bonding potential (e.g. when a thin glassy tube is inserted into mercury). Therefore, the meniscus will descend until this difference is compensated by gravitational potential.

2) When the meniscus descends, the lower gravitational potential of its molecules (compared to a flat surface) must be compensated by a higher bonding potential (*i.e.* less bonding). As a result, the meniscus is convex. Similar to 4.9 (a), the meniscus is not perfectly spherical.

#### 4.10. Thermocouple

A typical thermocouple is shown in **Figure 3** [7].

Suppose wire type A is made of Fe (iron), wire type B is made of Cu (copper), hot junction is at T, and the cold junction is fixed at  $0^\circ\text{C}$ ,  $V(T)$  denotes the electric potential in voltmeter. In this case, the total potential is the sum of molar chemical potential and  $V(T)$  (the gravitational potential can be neglected).



**Figure 3.** A typical measuring thermocouple (with a hot junction  $T$  and an electrical potential  $V(T)$  at the cold junction).

When two metals are connected at the hot junction  $T$  and a volt meter is connected at the cold junction, the following conditions would occur at equilibrium<sup>6</sup> based on the necessary and sufficient condition of the Atomistic 2<sup>nd</sup> Law of Thermodynamics:

- (a) At the common hot junction  $T$ , these two metals have equal total potential.
- (b) The temperature difference between hot junction and cold junction in two metals will result in a difference in molar chemical potential, respectively. When these metals also have a common cold junction, they will quickly generate an electric potential  $V(T)$  at the cold junction and reach equilibrium (because electrons can move quickly in metals). That is:

$$[\mu_{\text{Fe}}(0^\circ\text{C}) - \mu_{\text{Fe}}(T)] + V(T) = [\mu_{\text{Cu}}(0^\circ\text{C}) - \mu_{\text{Cu}}(T)] \quad (\text{Eq.25})$$

After rearrangement:

$$V(T) = \{[\mu_{\text{Cu}}(0^\circ\text{C}) - \mu_{\text{Cu}}(T)]\} - \{[\mu_{\text{Fe}}(0^\circ\text{C}) - \mu_{\text{Fe}}(T)]\} \quad (\text{Eq.26})$$

In (Eq.26), since  $\mu_{\text{Cu}}(0^\circ\text{C})$  and  $\mu_{\text{Fe}}(0^\circ\text{C})$  are constants,  $V(T)$  is related only to  $\mu_{\text{Cu}}(T)$  and  $\mu_{\text{Fe}}(T)$ . That is: when temperature  $T$  is changed, a corresponding  $V(T)$  is obtained. Therefore, after a calibration between  $V(T)$  and  $T$ , it is feasible to replace  $T$  with  $V(T)$ . The author believes this is the theoretical basis that a thermocouple can measure  $T$  based on  $V(T)$ .

Other types of thermocouple are with the same working principle, but the suitable working range of temperature is different. Hence the working principle of thermocouples is also closely related to the Atomistic 2<sup>nd</sup> Law of Thermodynamics.

## 5. Discussions

- (1) Kinetics should come first

The driving force of spontaneous evolution is the Atomistic 2<sup>nd</sup> Law of Ther-

<sup>6</sup>Since heat is one kind of kinetic energy, it should not be considered at equilibrium.

modynamics. The prerequisite is that the atomistic features can move. When there are kinetic constraints, the atomistic features are not able to move.

Consequently, kinetics would come first, while the atomistic 2<sup>nd</sup> Law of Thermodynamics is effective only when there are no kinetic constraints.

From observations, it is known that solid atomistic features are difficult to move. Hence, it is common that a solid system cannot reach equilibrium because of kinetic constraint. For example, oxides melted at high temperatures will form a liquid mixture. When this liquid mixture is slowly cooled down to room temperature, a mixture of oxide crystals will appear, having the lowest total chemical potential and the most stable structure. But when this liquid mixture is quickly cooled down to solid state, a glass is formed instead. This is because the oxide molecules do not have enough time moving to their equilibrium positions.

Another good example can be found in the phase transition between graphite and diamond [6]. At room temperature and pressure, the stable phase of carbon is graphite, while diamond is metastable (similar to glass). But diamond cannot transform to graphite at room temperature and pressure due to kinetic constraint. Because of this reason a diamond can exist forever at room temperature and pressure (like a glass).

A commonly observed example in steel industry is: when a melt of alloy steel is rapidly quenched into a solid steel, a metastable martensitic steel is formed due to the kinetic constraint. During tempering, the alloying elements in steel will have enough time moving to more stable positions and forming another structure.

Grain coarsening in solid materials is a commonly observed phenomenon at higher temperatures. It is also originated from the Atomistic 2<sup>nd</sup> Law of Thermodynamics, and the driving force is the higher chemical potential of the smaller grains. Its prerequisite is that solid molecules can move. This is why grain coarsening only happens at high temperatures (but the system is not yet at equilibrium).

Temperature is a means to measure heat energy. Its behavior, flowing from a higher point to a lower one, is similar to potentials. But the flowing of heat can be achieved by conduction, convection and radiation, therefore is more diversified. Probably for this reason, there are no apparent kinetic constraints for heat transfer.

## (2) Catalyst and activation energy

The use of catalysts can reduce the activation energy of a chemical reaction, therefore can increase its rate. But catalysts cannot change the concentrations of reactants and products. As mentioned earlier, the equilibrium constant  $K_{eq}$  of a chemical reaction is determined only by the concentrations and the molar numbers of reactants and products. Thus,  $K_{eq}$  is irrelevant to catalysts and activation energy.

There are reports indicating that due to a very high activation energy barrier [6] diamond will not transform to more stable graphite at room temperature and pressure. However, the author believes that this is not the reason. The real reason is that there is a kinetic constraint for the carbon atoms in diamond (similar to

the oxides in glass), which prevents them from reaching the most stable positions and transforming to graphite.

### (3) Why the atmosphere of Earth does not diffuse to outer space?

At the end of 4.5, the author reported that the atmosphere on Earth surface will diffuse to a vacuum chamber spontaneously. Then why the atmosphere of Earth does not diffuse to outer space (which is very close to vacuum)? The following explanation is based on the Atomistic 2<sup>nd</sup> Law of Thermodynamics, (Eq.14), and the gravitational potential of Earth:

In outer space, the gravitational potential for molar air molecules is  $(-G \cdot M \cdot m/r_1)$  [8], where  $G$  is the gravitational constant,  $M$  is the mass of Earth,  $m$  is the molar mass of air molecules,  $r_1$  is the distance from outer space to the center of Earth. Since the air concentration in outer space is  $\sim 0$ , (Eq.14) shows the  $\mu_G$  of air is  $-\infty^+$ . Consequently, the total potential of molar air molecules in outer space is  $(-G \cdot M \cdot m/r_1) + (-\infty^+)$ .

At the rim of the atmosphere on Earth [9], similar procedures show that the total potential of molar air molecules at the rim of atmosphere is  $(-G \cdot M \cdot m/r_2) + (-\infty^+)$ , where  $r_2$  is their distance from the rim of atmosphere to the center of Earth. Since this number is only slightly larger than that of outer space, there is no apparent driving force for the diffusion of atmosphere to outer space (very different from that on Earth surface).

But if numerous nuclear weapons were fired near the rim of atmosphere, the large amount of explosive energy [10] released by nuclear weapons would largely increase the temperature and pressure at the rim of atmosphere. It certainly would increase the kinetic energy of the air molecules in nearby atmosphere, thus would make them quickly diffuse to outer space. If the situation were severe enough, it would make many living things die. Human beings should be very cautious on this extremely dangerous scenario.

### (4) Atmosphere of Venus or Mercury

It is reported [11] that the surface temperature of Venus is  $\sim 462^\circ\text{C}$  and its surface pressure is  $\sim 92.1$  atm, both are far higher than Earth. According to the same report, at  $\sim 100$  kilometers away from Venus' surface, the atmosphere is only at  $-112^\circ\text{C}$  and  $0.00002660$  atm. These are not much different from Earth [9]. Therefore, it is expected that the atmosphere of Venus can also reach a balance with outer space, like Earth.

Another report [12] indicated that the atmosphere of Mercury is very thin (similar to Moon); and its pressure of atmosphere is about  $10^{-14}$  bar. It is unknown whether the original atmosphere of Mercury was very thin, or its original atmosphere was much thicker but almost all had diffused to outer space due to some reason.

### (5) Chemical potential and temperature

For a one component system with constant pressure and moles, it is known from the Classical 2<sup>nd</sup> Law of Thermodynamics that  $\partial\mu/\partial T = -S$  (*i.e.*  $\partial\mu = -S \cdot \partial T$ ), where  $T$  denotes temperature,  $S$  denotes molar entropy (always

larger than 0). As a result, when  $T$  increases, the molar chemical potential  $\mu$  will decrease, *i.e.* liquids will have lower bonding potentials and gases will have lower concentrations. The figure on moisture, liquid water, ice, and water solution by Martin Chapman [2] showed a similar trend but with more details (at 1 atm):

(a) For water vapor, liquid water and ice, their molar chemical potentials are all negative and all decrease as temperature increases (but with different slopes). The crossover points of these curves are the temperatures for the co-existence of two phases.

(b) Below the temperature of ice point, the chemical potential of ice is lower than the other two phases, therefore, ice is the most stable phase. For the same logic, water vapor is the most stable phase above boiling point, while liquid water is the most stable phase in between.

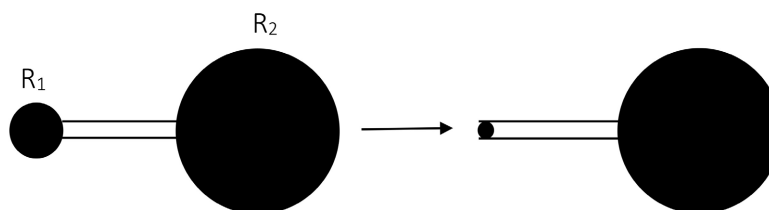
(c) The chemical potential of water molecules in water solutions is slightly lower than that of pure water. Therefore, the boiling point of water solution is slightly higher than  $100^{\circ}\text{C}$ . For the same reason, the ice point of water solution is slightly lower than  $0^{\circ}\text{C}$ . The latter can be applied to the routine of snow removal. Because the mixing of salt with ice will lower the ice point of mixture and make it easier to remove.

#### (6) Redox reactions [13]

Spontaneous redox reactions often occurred in solutions. If in standard condition the net electric energy change is positive for a redox reaction, then the reaction will release electric energy and occur spontaneously. This is equivalent to “the total potential energy of the reactants is lower”. Therefore, the spontaneous redox reactions also comply with the rule of Atomistic 2<sup>nd</sup> Law of Thermodynamics.

#### (7) Merging between small and large liquid drops

As shown in **Figure 4**,  $R_1$ ,  $R_2$  are the radii of liquid drops on the two sides of a tube. The small liquid drop will flow spontaneously and merge into the large liquid drop until total mergence. This is normally called the Young-Laplace phenomenon.



**Figure 4.** Spontaneous merging between small and large liquid drops.

Recently, the Young-Laplace phenomenon was studied based on a constant surface tension and the sizes of the liquid drops [14]. However, the interpretation of Young-Laplace phenomenon can be based on the Atomistic 2<sup>nd</sup> Law of Thermodynamics and its necessary and sufficient condition as follows (when kinetic constraint does not exist and there is no other driving force):

1) As shown in 4.1(a), the surface molecules in small liquid drop, having slightly

less bonding than large liquid drop, will have a slightly higher extra pressure  $\Delta P$  atm and a slightly higher chemical potential.

2) The higher chemical potential of small drop is the driving force for mergence. During merging the molar chemical potential of small drop will keep increasing, while the large drop is on the opposite. Hence, the driving force will keep increasing until the small drop totally merges into the large one. At the final mergence, the whole liquid drop will have the minimum chemical potential.

This phenomenon can be extended further:

1) If the large liquid drop is lifted up so that its lower molar chemical potential can be compensated by higher molar gravitational potential, then neither of the two drops will move (reach equilibrium). That is:

$$\mu_{R1} = \mu_{R2} + W \cdot h_0 \quad (\text{Eq.27})$$

In (Eq.27),  $\mu_{R1}$  and  $\mu_{R2}$  are the molar chemical potentials of small and large drops respectively;  $W$  denotes the molar weight of liquid drop;  $h_0$  denotes the extra height of large drop in order to be at equilibrium with the small one. Since  $W$  and  $h_0$  are both measurable,  $\mu_{R2}$  can be calculated from (Eq.27) once  $\mu_{R1}$  is obtained (vice versa).

2) If the large drop is further lifted up so that  $h_1 > h_0$ , then  $\mu_{R1} < \mu_{R2} + W \cdot h_1$  in (Eq.27). Under this circumstance:

The total potential of large drop becomes larger than that of small one. It is known from the necessary and sufficient condition of the Atomistic 2<sup>nd</sup> Law of Thermodynamics that the large drop will spontaneously merge into the small one. During mergence the large drop will gradually increase its chemical potential, while the small drop will be on the contrary. Hence, the driving force for this mergence will keep increasing until the large drop totally merges into the small one.

#### (8) Other driving forces

The Atomistic 2<sup>nd</sup> Law of Thermodynamics is a driving force toward spontaneous equilibrium. Other driving forces, however, will interfere with this driving force. Other driving forces are different from chemical potential, gravitational potential, electric potential, magnetic potential and etc. Because they are not originated from atomistic features, but are applied to atomistic features externally. For example, the  $\Delta P$  applied in a reverse osmosis system is a driving force of this kind. Similarly, the  $\Delta P$  applied outside or inside a capillary is also a driving force resulting in different meniscus height.

Plenty of tiny blood vessels (like capillaries) and membranes are in the body of an animal, therefore the aforementioned phenomena of capillary, osmotic pressure and reverse osmosis will be existing in animals. But the author believes, the heart of an animal is one kind of other driving forces. Hence, the phenomena of capillary, osmotic pressure and reverse osmosis inside animals will be different.

#### (9) Non-applicability of the Atomistic 2<sup>nd</sup> Law of Thermodynamics

The author believes that the Atomistic 2<sup>nd</sup> Law of Thermodynamics cannot be applied to the following conditions:

(a) When kinetic constraint exists: The prerequisite of the Atomistic 2<sup>nd</sup> Law of

Thermodynamics is “atomistic features can move”. Hence, this law cannot be applied to a system when its atomistic features cannot move due to kinetic constraint. For example, a glass or diamond at room temperature and pressure, quenched steel and etc.

(b) Not yet at equilibrium: It is possible that the system has not reached equilibrium because the moving speed of atomistic features is too low or the space is too wide. The examples include: the moisture contents in dark clouds are higher than its surroundings, and the composition of white clouds is different from the rest of sky. The moving speed of condensed features is much lower than that of gas features, therefore, the case of “not yet at equilibrium” is more pronounced in condensed systems. For example: different compositions are found in seawater around the world; grain coarsening in solid materials, etc.

(c) When other driving forces cannot be ignored: When other driving forces are important, the prediction relies solely on Atomistic 2<sup>nd</sup> Law of Thermodynamics would not be accurate any more. And the inclusion of other driving forces will get better results.

(d) When light plays an important role: Light energy is emitted by atomistic features. But these atomistic features are not at equilibrium state (at a steady state at most). Hence, the Atomistic 2<sup>nd</sup> Law of Thermodynamics is not applicable when light plays an important role. For example, the photosynthesis of plants on Earth, the phenomena in universe related to light and etc.

## 6. Conclusions

1. When a system evolves to a more stable state following the 2<sup>nd</sup> Law of Thermodynamics, it's through the movements of atomistic features. Thus, it's logical to study the 2<sup>nd</sup> Law of Thermodynamics based on the nature of atomistic features. This was the main reason why the author started working on the Atomistic 2<sup>nd</sup> Law of Thermodynamics.

2. For a simple system, a comparison between the Classical and the Atomistic 2<sup>nd</sup> Law of Thermodynamics has been made in **Table 1**. For this system, the rule of Atomistic 2<sup>nd</sup> Law of Thermodynamics is always “the total chemical potential  $N \cdot \mu$  is minimum”. While in Classical 2<sup>nd</sup> Law of Thermodynamics, one needs to use different parameters (*i.e.* S, E, H, F, G) for different system conditions. Since the former can be applied much more widely, it can be regarded as the widening of the latter.

3. Based on atomistic view, the 1<sup>st</sup> and 2<sup>nd</sup> Laws of Thermodynamics are described in Part 3. It is apparent that the 1<sup>st</sup> and 2<sup>nd</sup> Laws of Thermodynamics not only are closely related, but also both are simple and clear. The necessary and sufficient condition of the Atomistic 2<sup>nd</sup> Law of Thermodynamics is “the total potential of atomistic features is equal everywhere” (often encountered).

4. The molar total potential of atomistic features can be categorized as: (1) molar chemical potential: originated from the interaction among atomistic features; (2) other molar potentials: originated from the interaction between atomistic fea-

tures and environments (e.g. gravitational potential, electric potential, magnetic potential and etc.). It is worth noting that heat is one kind of kinetic energy, and is not needed for spontaneous evolutions toward equilibrium.

5. In liquid phase, the interaction among atomistic features is closely related to bonding. Therefore, the chemical potential of a liquid is determined by its bonding. In gas phase, since there is no bonding among atomistic features, the interaction and the molar chemical potential are likely dominated by its concentration.

6. In liquids, the chemical potential of atomistic features can be increased by pressure (like a pressed spring). As a result, the surface molecules (which have a higher bonding potential) will press inward and result in an extra pressure  $\Delta P_{\text{atm}}$  for inner molecules. Based on this concept, it is derived that the molar surface energy per unit surface area  $\gamma$  is proportional to the extra pressure  $\Delta P_{\text{atm}}$ , and simultaneously is inversely proportional to the surface area  $A$  of the water drop.

7. With the necessary and sufficient condition of the Atomistic 2<sup>nd</sup> Law of Thermodynamics, the phenomena of osmotic pressure and reverse osmosis are derived rigorously. The substances with aqua affinity or hydrophobicity are explained by “the total potential at interface is minimum”. Examples include lotus leaf, oil, water strider, etc. Due to the same reason, mercury will become a droplet on a wooden desk or a glass plate. This rule can also be applied to various surfactants and emulsifiers.

8. After some trials the author believes, the molar chemical potential of a gas phase can be expressed as  $\mu_G = k_0 \cdot \ln(k_{1G} \cdot [G])$ . But the values of  $k_0$  and  $k_{1G}$  are yet to be found. In deriving the equilibrium constant  $K_{eq}$  for the chemical reaction in gas phases represented by  $aA + bB \leftrightarrow cC + dD$ , only two conditions are used: (1)  $\mu_G = k_0 \cdot \ln(k_{1G} \cdot [G])$ , (2) the  $\sum N_i \cdot \mu_i$  of reactants is equal to the  $\sum N_j \cdot \mu_j$  of products (the same as  $\Delta G=0$  in the Classic 2<sup>nd</sup> Law of Thermodynamics).

9. In the derivation of  $K_{eq}$  for the chemical reaction in condensed phases represented by  $aA + bB \leftrightarrow cC + dD$ , one more condition is used: the condensed phases A, B, C, D are at equilibrium with their own gas phases. In this part, the Le Chatelier principle and the kinetic constraint are briefly mentioned. In addition, the feasibility of a chemical reaction or a phase change is reported. The examples used are the thermal disintegration of limestone and the phase transformation between graphite and diamond.

10. In 4.8, the author tried to describe the surface tension of a liquid based on the necessary and sufficient condition of the Atomistic 2<sup>nd</sup> Law of Thermodynamics. In 4.9, the capillary phenomenon is described rigorously based on the same rule. In 4.10, the working principle of a thermocouple is reported in detail.

11. The discussed topics are: kinetics should come first, catalyst and activation energy, why the atmosphere of Earth does not diffuse to outer space? Atmosphere of Venus or Mercury, chemical potential and temperature, redox reaction, other driving forces, merging between small and large liquid drops, non-applicability of the Atomistic 2<sup>nd</sup> Law of Thermodynamics. It is advisable to look into these dis-

cussions.

12. As a summary, at equilibrium the spontaneous physical phenomena and the spontaneous chemical reactions are all originated from the Atomistic 2<sup>nd</sup> Law of Thermodynamics. Perhaps because the applications of this law are very diversified, and many factors can interfere, it's not easy to connect all the related phenomena. The author believes it's time to have an atomistic view of thermodynamics laws, and make the 2<sup>nd</sup> Law of Thermodynamics simpler and more applicable.

Remarks:

The Atomistic 2<sup>nd</sup> Law of Thermodynamics is similar to many classical laws in that "having the characteristics of being easy to understand and easy to apply". The important classical laws include: Newton's first, second, and third laws, Newton's law of gravitation, Coulomb's law, Ohm's law, Faraday's law, Joule's law of electric heating, the 1<sup>st</sup> law of thermodynamics, the law of mass conservation,  $E = MC^2$ , and etc.

Although knowledge is very important, but "knowing what would happen but not knowing why it would happen" is not a good attitude for research. Because it has a negative influence on the accumulation of sciences and technologies, as well as on innovations. The author has tried to use "knowing why it would happen" in phenomena relating to the Atomistic 2<sup>nd</sup> Law of Thermodynamics. The author's hope is that some useful information could be provided to future researchers, and that the scientific world and students could all benefit.

## Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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