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Communication: Phenomena That Could Make the Atomistic 2nd Law of Thermodynamics Clearer

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Abstract

In the paper entitled "Communication: A Simpler and More Applicable 2nd Law of Thermodynamics", the author cited some well-known physical and chemical phenomena as well as speculations to elucidate that the Atomistic 2nd Law of Thermodynamics is simpler and more applicable. In the current communication, in addition to focusing on the experiments that could verify these speculations, some phenomena reported in literature are explained via the Atomistic 2nd Law of Thermodynamics and its related concepts. The reported subjects are: extra pressure ΔP inside a liquid drop, saturated vapor pressure and liquid curvature, surface energy of a liquid drop, molar chemical potential of a condensed phase, formula for the molar chemical potential of a gas, spontaneous merging between small and large liquid drops. Among these, the "surface energy of a liquid drop" is found to be $(\Delta P \cdot R)/3$ in which R is the radius of the liquid drop. Since this result and the related knowledge are different from current perception, a vigorous verification is required. In "molar chemical potential of a condensed phase", the categories of inter-molecular bonding are only briefly mentioned, and an in-depth study is needed. The discussed topics are: solubility of materials, solubility product of a compound, molar chemical potential and surface energy of a solid, constraints that should be fulfilled.

Keywords

Atomistic View, Chemical Potential, Bonding, Extra Pressure, Curvature of Liquid, Inter-Molecular Attraction, Capillary Condensation, Surface Energy, Concentration, Merging, Solubility Product, Sintering, Ostwald Ripening, Constraints

1. Introduction

In an article [1], Liu described the 2nd Law of Thermodynamics from an atomistic view and compared the Atomistic to the Classic 2nd Law of Thermodynamics for a simple system. Since the former has much wider applications, it can be regarded as the widening of the latter. Furthermore, from atomistic view it is apparent that the 1st and 2nd Laws of Thermodynamics are closely related to each other (very different from the classic thermodynamics).

In that communication, "the Atomistic 2nd Law of Thermodynamics and its necessary and sufficient condition" were applied to some well-known phenomena including: surface energy of a liquid drop, osmotic pressure and reverse osmoses, interfacial phenomena, capillary, thermocouple etc. Many topics were discussed, including kinetics should come first (e.g. explaining why metastable glass and diamond can exist forever at room temperature), catalyst and activation energy, chemical potential and temperature, non-applicability of the Atomistic 2nd Law of Thermodynamics etc.

However, there were speculations in that paper based on the Atomistic 2nd Law of Thermodynamics and its necessary and sufficient condition. For example, the extra pressure ΔP inside a liquid drop, the surface energy of a liquid drop, the formula for the molar chemical potential of a gas, the merging between small and large liquid drops at two ends of a tube and etc. The main focus of the current communication is to verify some of these speculations, hoping someone could prove these phenomena experimentally. In addition, some phenomena reported in literature are explained based on the Atomistic 2nd Law of Thermodynamics and its related concepts, with the aim to make this law clearer.

2. Important Elucidating Phenomena

The important phenomena that could make the Atomistic 2nd Law of Thermodynamics clearer include the following:

2.1. Extra Pressure ΔP Inside a Liquid Drop

The author believes that the chemical potential of liquid molecules is dominated by their bonding with the same kind molecules. A liquid drop can be roughly divided as surface molecules and inner molecules. The inner molecules will have an extra pressure ΔP due to the following reasons:

a) With the perception that "bonding potential is negative", the bonding potential of inner molecules is more negative because of more bonding. That is, their molar chemical potential is lower than that of surface molecules when both are at 1 atm.

b) The molar chemical potential of molecules can be increased by an extra pressure ΔP (similar to a pressed spring).

c) When the liquid drop is at equilibrium, the molar chemical potential of inner molecules must be the same as that of surface molecules. Therefore the inner molecules should have an extra pressure ΔP (in other words, surface molecules will

press inward resulting in the extra pressure ΔP).

The smaller is the liquid drop, the less complete is the bonding of surface molecules. Hence the higher is ΔP. The ΔP inside a liquid drop is very essential to the Atomistic 2nd Law of Thermodynamics. If someone can verify the existence of ΔP (which should be far smaller than 1 atm) and that ΔP increases with decreasing radius of the liquid drop, it certainly will make the Atomistic 2nd Law of Thermodynamics clearer.

2.2. Saturated Vapor Pressure and the Liquid Curvature on Surface

In the book "Physics and Chemistry of Interfaces", Butt *et al.* described: the saturated vapor pressure of a liquid drop is higher than that of a flat surface [2]. This phenomenon can be shown graphically in **Figure 1**:

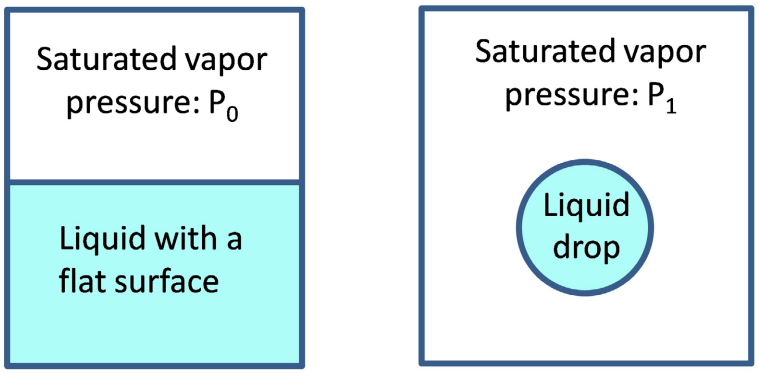

Figure 1. The saturated vapor pressure of a liquid drop is higher than that of a flat surface (*i.e.* $P_1 > P_0$).

The author's explanation of this phenomena is: the surface of a liquid drop is convex which results in less bonding and a higher molar chemical potential for the surface molecules. Thus a liquid drop will have a higher saturated vapor pressure (compared to a liquid with flat surface). Landau *et al.* also reported a similar phenomenon that the saturated vapor pressure above a drop of liquid increases with decreasing radius of the drop [3]. All these phenomena can be explained by the differences in liquid curvature at surface.

Similarly, the descending meniscus in a capillary has a convex surface and the surface molecules have a higher molar chemical potential than a flat surface, thus this meniscus also has a higher saturated vapor pressure [3]. The above-mentioned phenomena can be extended further: It may happen that the vapor is supersaturated with respect to the larger droplets but unsaturated with respect to the smaller ones. Then the liquid which evaporates from the smaller drops will condense on the larger ones, which as it were "consume" the small drops [3].

Conversely, when liquids have concave surfaces, the phenomena on saturated vapor pressure are totally opposite, as also reported in literature [2]-[5], examples include:

a) The liquid surfaces surrounding gas bubbles are concave, resulting in lower molar chemical potentials and lower saturated vapor pressures inside gas bubbles.

b) The surface of a rising meniscus in capillary is concave, thus it also has a lower saturated vapor pressure than a flat surface. For this reason the vapor generated from flat surface would diffuse to and condense on the meniscus surface (called capillary condensation).

c) The higher does the meniscus rise in capillary, the more is gravitational potential needed for its equilibrium. Hence the lower is the molar chemical potential of the meniscus and the more pronounced is the capillary condensation.

Capillary condensation is also observed in solids with small pores which will act like capillaries. For example, capillary condensation would occur in soil, shales, building materials, man-made foods, thus making these small pores have some condensed liquids [4]-[7].

Based on the various phenomena mentioned, it can be deduced that the curvature of liquid surface, whether it's flat, convex or concave, is the main factor determining the saturated vapor pressure. And the larger is the curvature of liquid surface, the more different is the saturated vapor pressure from that of a flat surface. Although this induction complies with the perception that the molar chemical potentials of liquid molecules originate from bonding, more verifications and better descriptions are needed.

2.3. Surface Energy of a Liquid Drop

When gravitational potential can be neglected, for a liquid drop at room temperature and 1 atm, its molar chemical potential at surface, $\mu(1)_{\text{surface}}$, can be defined as:

$$\mu(1)_{\text{surface}} = \mu(1)_{\text{inner}} + \gamma(1)\cdot A \tag{1}$$

In Equation (1), $\mu(1)_{\text{inner}}$ is the molar chemical potential of inner molecules at 1 atm, "$\gamma(1)\cdot A$" is the excess molar potential due to the convex surface of liquid drop at 1 atm. Here $\gamma(1)$ is defined as the excess energy per unit surface area of the liquid drop at 1 atm (the same as traditional definition), "A" is defined as the molar surface area of the liquid drop.

When the inner molecules of liquid drop are at equilibrium with its surface molecules, the necessary and sufficient condition of the Atomistic 2nd Law of Thermodynamics requires that $\mu(1)_{\text{surface}}$ is equal to $\mu(1 + \Delta P)_{\text{inner}}$. Here ΔP is defined as the extra pressure of the inner molecules at 1 atm. Based on this condition, the author has derived the following Equation for 1 atm [1] (in its Equation (7)):

$$\gamma(1) \fallingdotseq \left[\Delta P \cdot v(1)\right] \div A \tag{2}$$

In Equation (2), $v(1)$ is the molar volume of liquid at 1 atm, defined as $v(1) = M \div \rho(1)$ where M is the molar weight of liquid drop and $\rho(1)$ is its density at 1 atm.

When R is the radius of the liquid drop, its surface area is $4\pi R^2$ and its volume is $(4\pi R^3/3)$, where π is the circular ratio. The number of moles in this liquid drop is $(4\pi R^3/3)\cdot\rho(1) \div M$. Hence, "$A$", defined as the molar surface area of the liquid drop, is equal to the surface area of this liquid drop divided by its moles, *i.e.*:

$$\begin{aligned} A &= 4\pi R^2 \div \left[\left(4\pi R^3/3 \right) \cdot \rho(1) \div M \right] \\ &= (3/R) \cdot \left(M \div \rho(1) \right) \\ &= (3/R) \cdot v(1) \end{aligned} \tag{3}$$

Plug Equation (3) into Equation (2), we'll get:

$$\gamma(1) \fallingdotseq (\Delta P \cdot R)/3 \tag{4}$$

Equation (4) implies:

a) Surface energy $\gamma(1)$ can be calculated once ΔP and R are obtained. This is different from the conventional way to obtain surface energy $\gamma(1)$.

b) The value ($\Delta P \cdot R$) of a liquid drop is not necessarily a constant when R changes, neither is its surface energy $\gamma(1)$.

c) When R is fixed, the surface energy at 1 atm, $\gamma(1)$, is proportional to the extra pressure ΔP.

Since there is no special condition in the derivation of (Equation (4)), this result should be applicable to all materials. Due to the fact that (a), (b) are different from conventional knowledge, a rigorous verification of (Equation (4)) is necessary.

If Equation (4) is correct, it should contribute considerably to the rationalization of surface energies for materials. If Equation (4) is mistaken, the reasons for being mistaken should be studied for a better understanding. Furthermore, when the liquid drop is under a pressure different from 1 atm, the relation between γ and pressure would be interesting, so is the relation between ΔP and pressure.

2.4. Molar Chemical Potential of a Condensed Phase

In Classic 2nd Law of Thermodynamics, the molar chemical potential of component i is defined as "the increase in Gibbs free energy due to the addition of one mole of component i, when temperature, pressure and other molecules are fixed". This definition is relative in nature and it does not mention the origin of molar chemical potential. Since the molar chemical potential of material is the core of the Atomistic 2nd Law of Thermodynamics when Liu developed this law, a study on the origin of chemical potential is reasonable.

In literature, Cook *et al.* [8], Baierlein [9], Job *et al.* [10] all tried to study in-depth the molar chemical potentials of materials, but it seemed that they did not have much success. Their comments can be summarized as: "students generally could not perceive the meaning of molar chemical potential, yet it can be applied widely to physical and chemical phenomena". After searching, it's also not possible for the author to find the origin of molar chemical potential in Wikipedia, google or DeepSeek.

The author believes, chemical potential is originated from the interaction among molecules of the same kind. In a condensed phase of one component, this interaction is dominated by inter-molecular bonds. According to Wikipedia, these inter-molecular bonds can be categorized as [11]: 1) ionic bond, 2) covalent bond, 3) hydrogen bond, 4) dipole bond, 5) London dispersion forces (commonly called Van der Waal forces).

From the same source, the relative strength of these inter-molecular bonds were differentiated in a table[1]: ionic bond is the strongest, covalent bond is the next, while the rest 3 bonds (sometimes all called Van der Waal forces) are the weakest [11]. However, metallic bond is not in this table. From known information, most metals are with relative high melting points (except mercury). Their boiling points are even higher. These facts indicate that the attraction force of the metallic bonds are very strong.

If the molar chemical potentials of condensed phases could be categorized according to the above-mentioned inter-molecular bonds, it should help the progress in the advance of material physics and chemistry. The same is true if extra pressure ΔP and the surface energy γ of a liquid drop could also be categorized based on these inter-molecular bonds.

2.5. Formula for the Molar Chemical Potential of a Gas

In the region where a liquid is at equilibrium with its own gas, both phases have the same molar chemical potential. Therefore it's not difficult to know the molar chemical potential of a gas experimentally. However, if the molar chemical potential of a gas can be expressed as a formula, the applications will be much wider and the convenience much better. For this reason, it's worth a deep look at the formula for the molar chemical potential of a gas.

All gas molecules are free to move in open space, hence their bonding potentials should be zero. With the perception that chemical potential is originated from the interaction among molecules of the same kind, it can be inferred that the formula of molar chemical potential of a gas should be dominated by its molar concentration. While the well-known phenomena related to gases would serve as the constraints of this formula[2]. After trials, the author came up with the following formula for the molar chemical potential μ_G of a gas G:

$$\mu_G = k_0 \cdot \ln\left(k_{1G} \cdot [G]\right) \tag{5}$$

In Equation (5), $[G]$ is the molar concentration of the gas G; k_0 is a positive constant for every material which only depends on temperature and pressure; k_{1G} is a constant not only dependent on temperature and pressure, but also dependent on gas G; $k_{1G}[G]$ is without unit and $0 \le k_{1G} \cdot [G] < 1$.

As the author have said in the conclusions 8 of reference [1]: the values of k_0 and k_{1G} are yet to be determined. In this communication, the author proposes a procedure to determine the values of k_0 and k_{1G}, and proposes the methods to verify whether these values are reasonable and consistent.

The following is taking the equilibrium of $aA + bB \leftrightarrow cC + dD$ as an example

[1]According to Wikipedia, this table was partly cited from: 1) Organic Chemistry (2004): Structure and Reactivity (5th ed.), Boston: Houghton Mifflin Company. pp.30-33, 67. 2) *Lattice Energy,* Purdue University. Retrieved 2014-01-21. 3) Majer V, Svoboda V (1985), Enthalpies of Vaporization of Organic Compounds.

[2]The constraints include: 1) The molar chemical potential of gas must be negative, so that it can equal to that of its liquid. 2) The higher is the gas concentration, the higher is the molar chemical potential of gas, so that the gas will diffuse to a place with a lower concentration. 3) The equilibrium constant K_{eq} of $aA+bB \leftrightarrow cC+dD$ must be $([C]^c \cdot [D]^d) \div ([A]^a \cdot [B]^b)$.

(a, b, c, d are the moles of gases A, B, C, D respectively). According to Equation (5), μ_A,μ_B, μ_C, μ_D can be expressed as:

$$\begin{aligned} \mu_A &= k_0 \cdot \ln\left(k_{1A} \cdot [A]\right),\ \mu_B = k_0 \cdot \ln\left(k_{1B} \cdot [B]\right) \\ \mu_C &= k_0 \cdot \ln\left(k_{1C} \cdot [C]\right),\ \mu_D = k_0 \cdot \ln\left(k_{1D} \cdot [D]\right) \end{aligned} \tag{6}$$

In Equation (6), [A], [B], [C], [D] are the molar concentrations of gases A, B, C, D respectively.

a) To determine the values of k_0 and k_{1A}, k_{1B}, k_{1C}, k_{1D}

When $aA + bB \leftrightarrow cC + dD$ spontaneously reaches equilibrium, the total chemical potential of reactants N_b, *i.e.* $\sum N_i \cdot \mu_i$, must be equal to the total chemical potential of products N_f, *i.e.* $\sum N_j \cdot \mu_j$, hence:

$$a \cdot \mu_A + b \cdot \mu_B = c \cdot \mu_C + d \cdot \mu_D \tag{7}$$

Plug Equation (6) into Equation (7) and after some treatments, we'll derive (for details, please see the derivation of (Equation (20)) in [1]):

$$\left(k_{1A}^a \cdot k_{1B}^b\right) \div \left(k_{1C}^c \cdot k_{1D}^d\right) = \left([C]^c \cdot [D]^d\right) \div \left([A]^a \cdot [B]^b\right) \tag{8}$$

Since Equation (6) can be rewritten as:

$$\begin{aligned} k_{1A} &= \left[\mathrm{e}^{(\mu_A \div k_0)}\right] \div [A],\ k_{1B} = \left[\mathrm{e}^{(\mu_B \div k_0)}\right] \div [B] \\ k_{1C} &= \left[\mathrm{e}^{(\mu_C \div k_0)}\right] \div [C],\ k_{1D} = \left[\mathrm{e}^{(\mu_D \div k_0)}\right] \div [D] \end{aligned} \tag{9}$$

We can plug Equation (9) into Equation (8) and derive:

$$\begin{aligned} &\left(\left\{\mathrm{e}^{(\mu_A \div k_0)} \div [A]\right\}^a \cdot \left\{\left[\mathrm{e}^{(\mu_B \div k_0)}\right] \div [B]\right\}^b\right) \div \left(\left\{\left[\mathrm{e}^{(\mu_C \div k_0)}\right] \div [C]\right\}^c \cdot \left\{\left[\mathrm{e}^{(\mu_D \div k_0)}\right] \div [D]\right\}^d\right) \\ &= \left([C]^c \cdot [D]^d\right) \div \left([A]^a \cdot [B]^b\right) \end{aligned} \tag{10}$$

In Equation (10), when the temperature and pressure are fixed, the numeric value of [A], [B], [C], [D], a, b, c, d are known values from experiment; if the reliable values of μ_A, μ_B, μ_C, μ_D are obtainable, the only unknown is k_0. With current computational capability, the numeric value of k_0 can be calculated from Equation (10) without much difficulty. Once the numeric value of k_0 is obtained, the corresponding numeric values of k_{1A}, k_{1B}, k_{1C}, k_{1D} can be calculated from Equation (6).

b) Verify if k_{1A}, k_{1B}, k_{1C}, k_{1D} are reasonable

Experimentally, it is known that the equilibrium constant for $aA + bB \leftrightarrow cC + dD$ can be expressed as [12]:

$$K_{eq} = \left([C]^c \cdot [D]^d\right) \div \left([A]^a \cdot [B]^b\right) \tag{11}$$

Once k_{1A}, k_{1B}, k_{1C}, k_{1D} are obtained, the value of $\left(k_{1A}^a \cdot k_{1B}^b\right) \div \left(k_{1D}^c \cdot k_{1D}^d\right)$ can be calculated for the left-hand side of Equation (8). Hence under different temperature and pressure, whether or not the values of $\left(k_{1A}^a \cdot k_{1B}^b\right) \div \left(k_{1D}^c \cdot k_{1D}^d\right)$ are equal to $\left([C]^c \cdot [D]^d\right) \div \left([A]^a \cdot [B]^b\right)$ [3] is a means to verify if k_{1A}, k_{1B}, k_{1C}, k_{1D} are reasonable.

[3]In other words, whether Equation (8) is valid under various temperatures and pressures.

c) Verify the consistencies of k_0, k_{1A}, k_{1B}, k_{1C}, k_{1D}

If gas A has chemical reactions other than $aA+bB \leftrightarrow cC+dD$, then k_0 and k_{1A} can also be obtained from other chemical reactions (the prerequisite is the related molar chemical potentials are reliable). If all the obtained k_0 and k_{1A} are consistent for all the chemical reactions involving gas A, then Equation (5) is applicable to gas A.

If gases B, C, D have chemical reactions other than $aA+bB \leftrightarrow cC+dD$, then k_0 and k_{1B}, k_{1C}, k_{1D} can also be obtained via other chemical reactions. In these cases, the following should be verified:

1) Whether the k_0 and k_{1B}, k_{1C}, k_{1D} obtained are consistent for all the chemical reactions involving gases B, C, D.

2) Whether the k_0 obtained is the same as that obtained from gas A.

If all k_0, k_{1G} are reasonable and consistent, it implies that Equation (5) (where k_0, k_{1G} are from) are also reasonable. Under this condition, whether or not k_0, k_{1G} can be simplified as formulas is a topic needing study. On the other hand, if k_0, k_{1G} are not reasonable or not consistent after rigorous verifications, it is likely that Equation (5) is not the correct formula for the molar chemical potential of a gas. In this case, to look into the reasons and to find a better formula are the logical next steps.

2.6. Spontaneous Merging Between Small and Large Liquid Drops

Based on the Atomistic 2nd Law of Thermodynamics and its necessary and sufficient condition, Liu [1] had discussed the spontaneous merging between small and large liquid drops at the two ends of a horizontal tube. Via speculations, this phenomenon was extended to the conditions when the heights of liquid drops are different. These conditions can be shown more clearly in Figures 2(a)-(d):

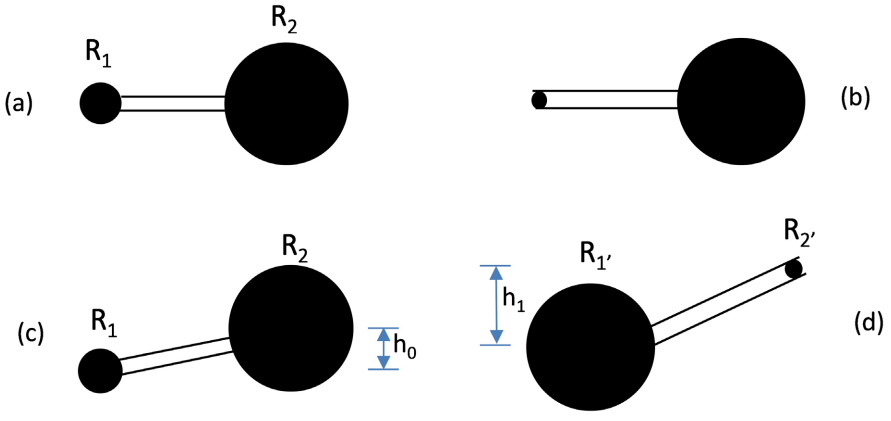

Figure 2. The spontaneous mergeing between small and large liquid drops at the two ends of a tube.

Figure 2(a) is the initial state when the small and large liquid drops are connected through a hollow and horizontal tube. Figure 2(b) is in the midway when the small liquid drop is merging toward the large one. Figure 2(c) shows that when the large liquid drop is lifted up with a height h_0 so that the total molar

potentials (*i.e.* the sum of molar chemical potential and molar gravitational potential) of the two drops are equal, therefore neither drop will move. In **Fig. 2(d)**, the large liquid drop is lifted further with a height h_1 ($h_1 > h_0$), so that the large liquid drop is spontaneously merging into the small one.

The phenomena in Figure 2 are based on speculations, and the molar gravitational potentials of liquid drops are involved. If someone could verify Figure 2 experimentally, it would confirm that the Atomistic 2nd Law of Thermodynamics and its necessary and sufficient condition are applicable to these phenomena.

3. Discussions

3.1. Solubility of Materials

If the potentials other than chemical potential can be neglected, whether a material can be dissolved in a solvent is determined by that whether or not the total chemical potential of the system can be reduced. If the dissolution of a material will result in a decrease of the total chemical potential, then this material will keep dissolving until saturation is reached or the solid solvent has exhausted (e.g. salt in water).

At saturation the molar chemical potential of the solute is equal to that of the co-existing phases, e.g., the molar chemical potential of the salt dissolved in water is equal to that of the solid salt in water. Another example is that the molar chemical potential of the oxygen dissolved in water is equal to that of the oxygen in air.

If the molar chemical potential of a solute is higher than that of its saturated value due to condition change, then part of the solute will leave the solution. Examples include: salt will crystalize from largely condensed sea water, or the dissolved oxygen in a pond will decrease because of temperature rise. These phenomena certainly comply with the Atomistic 2nd Law of Thermodynamics or its necessary and sufficient condition.

If the dissolution of a material will result in an increase of total chemical potential in the system, then this material will not dissolve at all, e.g. sand, metals, glass or woods in water. Also, oils are generally insoluble in water. On the other hand, experiments showed that all gases can dissolve in water to certain extents, while the least soluble gas is Helium [13]. Hence, it's logical to expect that the total chemical potential of the system be reduced when gases dissolve in water.

3.2. Solubility Product of a Compound

When a compound A_pB_q dissolves in solvent X via the reaction $A_pB_q \leftrightarrow pA_{(sol.)} + qB_{(sol.)}$, it makes sense that its equilibrium condition is similar to the chemical reaction of gases $aA + bB \leftrightarrow cC + dD$. Since the equilibrium condition for $aA + bB \leftrightarrow cC + dD$ is $\sum N_i \cdot \mu_i = \sum N_j \cdot \mu_j$ (i denotes reactants, j denotes products), it's logical to expect that the equilibrium condition for $A_pB_q \leftrightarrow pA_{(sol.)} + qB_{(sol.)}$ would be:

$$\mu\left(A_pB_q\right) = p \cdot \mu\left(A_{(sol.)}\right) + q \cdot \mu\left(B_{(sol.)}\right) \tag{12}$$

In Equation (12), $\mu(A_pB_q)$ is the molar chemical potential of the compound A_pB_q, while $\mu(A_{(sol.)})$ and $\mu(B_{(sol.)})$ are the molar chemical potentials of components A and B in solution respectively; p and q are the molar numbers of A and B in solution. The concept that "chemical potential is originated from the interaction among the same molecules" should also be applicable to solutions. Hence $\mu(A_{(sol.)})$ and $\mu(B_{(sol.)})$ are dominated by molar concentrations $[A]$ and $[B]$, and their formulas are likely:

$$\mu\left(A_{(sol.)}\right)=k_2\cdot\ln\left(k_{3A}\cdot[A]\right),\ \mu\left(B_{(sol.)}\right)=k_2\cdot\ln\left(k_{3B}\cdot[B]\right) \tag{13}$$

Equation (13) is similar to the formula of the molar chemical potential of a gas (but with different constants). In Equation (13), k_2 (with the same unit as μ) is a positive constant common to all solutes in solvent X, and is dependent on temperature and pressure. While k_{3A} or k_{3B} (with the unit of concentration^{-1}) not only is dependent on temperature and pressure, but also is dependent on solvent X and solute A or B.

Similar to the formulas of the molar chemical potential of gases, the values of k_2, k_{3A} and k_{3B} can be determined and verified via the following procedures:

a) To determine the values of k_2 and k_{3A}, k_{3B}

Plug Equation (13) into Equation (12), we'll get:

$$\mu\left(A_pB_q\right)=p\cdot k_2\cdot\ln\left(k_{3A}\cdot[A]\right)+q\cdot k_2\cdot\ln\left(k_{3B}\cdot[B]\right) \tag{14}$$

Now moving the common factor k_2 from right-side to left-side, and moving p, q inside of ln, Equation (14) becomes:

$$\mu\left(A_pB_q\right)\div k_2=\ln\left(k_{3A}\cdot[A]\right)^p+\ln\left(k_{3B}\cdot[B]\right)^q \tag{15}$$

Taking both sides of Equation (15) as the exponent of natural logarithm, Equation (15) becomes:

$$\mathrm{e}^{\mu\left(A_pB_q\right)\div k_2}=\left(k_{3A}\cdot[A]\right)^p\cdot\left(k_{3B}\cdot[B]\right)^q \tag{16}$$

After moving $(k_{3A})^p$ and $(k_{3B})^q$ to the left-side of Equation (16), we can derive:

$$\mathrm{e}^{\mu\left(A_pB_q\right)\div k_2}\div\left[\left(k_{3A}\right)^p\cdot\left(k_{3B}\right)^q\right]=[A]^p\cdot[B]^q \tag{17}$$

Now expressing k_{3A} and k_{3B} in terms of k_2 in Equation (13):

$$k_{3A}=\mathrm{e}^{\mu\left(A_{(sol.)}\right)\div k_2}\div[A],\ k_{3B}=\mathrm{e}^{\mu\left(B_{(sol.)}\right)\div k_2}\div[B] \tag{18}$$

Plugging Equation (18) into the k_{3A} and k_{3B} of Equation (17), we'll derive:

$$\mathrm{e}^{\mu\left(A_pB_q\right)\div k_2}\div\left[\left(\mathrm{e}^{\mu\left(A_{(sol.)}\right)\div k_2}\div[A]\right)^p\cdot\left(\mathrm{e}^{\mu\left(B_{(sol.)}\right)\div k_2}\div[B]\right)^q\right]=[A]^p\cdot[B]^q \tag{19}$$

In Equation (19), when the temperature, pressure and solvent are fixed at equilibrium, the numeric values of $[A]$, $[B]$, p, q are known. If the reliable values of $\mu(A_pB_q)$, $\mu(A_{(sol.)})$ and $\mu(B_{(sol.)})$ are available, then k_2 is the only unknown in Equation (19). Hence it's not difficult to determine k_2 from Equation (19) under current calculating capability. Once the value of k_2 is determined, the numeric values

of the corresponding k_{3A} and k_{3B} can be calculated from Equation (13).

b) To verify if k_2, k_{3A}, k_{3B} are reasonable

Experimentally the solubility product K_{sp} of $A_pB_q \leftrightarrow pA_{(sol.)} + qB_{(sol.)}$ can be expressed as [14]:

$$K_{sp} = [A]^p [B]^q \tag{20}$$

Once the value of k_2, k_{3A}, k_{3B} are determined, the value of $e^{\mu(A_pB_q)\div k_2} \div \left[(k_{3A})^p \cdot (k_{3B})^q \right]$ for this dissolution can be calculated. At various temperatures and pressures "whether or not the values of $e^{\mu(A_pB_q)\div k_2} \div \left[(k_{3A})^p \cdot (k_{3B})^q \right]$ are equal to $[A]^p[B]^q$ (*i.e.* the experimental K_{sp})"[4] is a means to verify that if k_2, k_{3A}, k_{3B} are reasonable.

c) To verify if the values of k_2, k_{3A}, k_{3B} are consistent

If component "A" can dissolve in solvent X through other reactions, then k_2 and k_{3A} can also be obtained through other dissolutions. In this case, all the k_2 and k_{3A} should be consistent. Otherwise Equation (13) cannot be the right formula for the molar chemical potential of component "A" in solvent X. Similarly for component "B" or other solvent.

If k_2, k_{3A}, k_{3B} are reasonable and consistent in all dissolutions, it implies that Equation (13) is also reasonable. Under this condition, whether or not k_2, k_{3A} and k_{3B} can be simplified as formulas is a topic needs further study. On the other hand, if k_2, k_{3A}, k_{3B} are not reasonable or not consistent in all dissolutions, it is likely that Equation (13) is not the correct formula for the molar chemical potential of solute, and a better formula should be looked for.

When a solid dissolves, its solubility product K_{sp} is normally defined for large monocrystals [15]. From experiments, it is known that K_{sp} will become larger when the grain size of this solid decreases [16] [17]. This phenomenon certainly complies with the perception that the molecules of smaller grains are with less complete bonding at surface, thus have a higher molar chemical potential and a larger K_{sp}.

When two solids with a common ion can both be dissolved in a solvent (e.g. the Cl^- in $PbCl_2$ and NaCl dissolved in water), experiments showed that the solubility products of both solids will basically remain unchanged. Since the solubility of NaCl is much higher than that of $PbCl_2$ in water, the $[Na^+]$ and $[Cl^-]$ will be high and $[Pb^{2+}]$ will be very low [18].

3.3. Molar Chemical Potential and Surface Energy of a Solid

At certain temperature and pressure when a solid is at equilibrium with its liquid, the molar chemical potentials of both phases are equal. Hence it's not difficult to obtain the molar chemical potential of a solid experimentally.

When there are defects (e.g. dislocations) or residue stresses (e.g. in metal forming, welding or distorted solids) in a solid, theoretically the molar chemical po-

[4]In other words, whether Equation (17) is valid under various temperatures and pressures.

tential of this solid will increase. Similarly, when the crystals of a solid are very small, the molar chemical potential will increase due to largely increased interfaces. Under these conditions, the molar chemical potentials of solids will be higher than they should. Hence it is advisable to minimize interferences as much as possible when measuring the molar chemical potentials of solids.

As to the surface energy of a single-crystal solid, attention should be paid to the direction of the surface plane, because it will make substantial difference. For example, according to the table of Wikipedia [19], the surface energy is 300 mJ/m^2 when the surface plane of NaCl is (100). While the surface energy is changed to 400 mJ/m^2 when the surface plane of NaCl becomes (110). In general, polycrystalline solids are more commonly encountered. Their surface energies can be taken as the average of all planes.

Smaller grains in solids have higher surface energies and higher molar chemical potentials. According to the Atomistic 2nd Law of Thermodynamics, the higher surface energies will become driving forces for the small grains to grow spontaneously, provided the temperature is high enough so that molecules can move. Examples include sintering processes and Ostwald Ripening in solid solutions [20]-[22].

3.4. Constraints That Should Be Fulfilled

When conducting experiments or developing formulas to make the Atomistic 2nd Law of Thermodynamics clearer, there should be certain constraints to be fulfilled. These reasonable constraints include:

a) To avoid the conditions that the Atomistic 2nd Law of Thermodynamics is not applicable: As addressed in [1], the conditions that the Atomistic 2nd Law of Thermodynamics is not applicable include: 1) when there are kinetic constraints, 2) when the system is not yet at equilibrium, 3) when other driving forces cannot be ignored, 4) when light energy plays an important role.

b) The developed concepts or formulas should comply with the known experimental results: Example include:

1) The bonding conditions at liquid surfaces should comply with their saturated vapor pressures in observations (including capillary condensation);

2) The formulas for the molar potential of a gas should comply with the known phenomena (as described in footnote 2);

3) In the chemical reaction of gases via $aA+bB \leftrightarrow cC+dD$, the calculated K_{eq} based on k_{1A}, k_{1B}, k_{1C}, k_{1D} (*i.e.* $\left(k_{1A}^{a} \cdot k_{1B}^{b}\right) \div \left(k_{1C}^{c} \cdot k_{1D}^{d}\right)$) should be the same as the experimental K_{eq};

4) For a compound dissolved in a solvent via $A_pB_q \leftrightarrow pA_{(sol.)} + qB_{(sol.)}$, the calculated K_{sp} based on $\mu(A_pB_q)$ and k_2, k_{3A}, k_{3B} (*i.e.* $e^{\mu\left(A_pB_q\right) \div k_2} \div \left[\left(k_{3A}\right)^p \cdot \left(k_{3B}\right)^q\right]$) should be the same as the experimental K_{sp}.

c) The constants obtained for the same formula should be consistent: For example, 1) If k_0 and k_{1G} can be obtained from various chemical reactions, then all

the constants k_0 and k_{1G} should be consistent (as described in Section 2.5). 2) Similarly, if k_2 and k_{3A}, k_{3B} can be obtained from various dissolutions in the same solvent, then all the k_2 and k_{3A}, k_{3B} should also be consistent (as described in Section 3.2).

4. Conclusions

1) The inner molecules of a liquid drop have more complete bonding and lower molar chemical potential than surface molecules. To be at equilibrium with the surface molecules, the inner molecules must have an extra pressure ΔP to increase their molar chemical potential. If verifications can be made for the existence of ΔP and that ΔP increases as the radius of the liquid drop decreases, they would contribute to better knowledge of the Atomistic 2nd Law of Thermodynamics.

2) The various phenomena related to the saturated vapor pressure of a liquid are originated from the bonding conditions of surface molecules, whether the liquid is with a flat surface or a curved surface. Examples include a liquid drop, a rising or descending meniscus in capillary, gas bubbles in liquid, capillary condensation (including the liquid condensed in pores) etc. With the same logic, when small water drops are together with large ones, the former will keep evaporating due to under-saturation, while the latter will keep condensing due to over-saturation.

3) At 1 atm, for a liquid drop with radius R and extra pressure ΔP, its surface energy $\gamma(1)$ is found to be $(\Delta P \cdot R)/3$. This formula implies: (a) Once ΔP and R are obtained, $\gamma(1)$ can be calculated. (b) When R changes, $\gamma(1)$ is not necessarily a constant. (c) When R is fixed, $\gamma(1)$ is proportional to ΔP. Since these implications are different from the conventional perceptions on surface energy, a rigorous verification is necessary. Moreover, the relations between γ and pressure (or ΔP and pressure) is worth studying.

4) The origin of molar chemical potential is not reported, possibly due to the difficulties involved. With the perception that "the molar chemical potentials of a condensed phase is originated from inter-molecular bonding", the author studied in a primitive way about the 6 categories of inter-molecular bonds. It is hoped that someone can investigate into this topic furthermore. If the molar chemical potential of materials (or ΔP, γ) can be related to these 6 categories, they could contribute to the advances in materials physics and chemistry.

5) In previous communication, the author has proposed that the formula for the molar chemical potential of a gas is $\mu_G = k_0 \cdot \ln\left(k_{1G} \cdot [G]\right)$. In this communication, the author suggests a procedure to find the values of k_0 and k_{1G}. When k_0 and k_{1G} are obtained, an important verification is: whether or not the calculated K_{eq} (based on k_0 and k_{1G}) is equal to the experimental $K_{Eq.}$ In addition, if k_0 and k_{1G} can be obtained from other chemical reactions, all the k_0 and k_{1G} should be consistent. Otherwise, a better formula should be looked for.

6) Regarding the spontaneous merging between small and large liquid drops at the two ends of a hollow tube, the author had some speculations based on the

Atomistic 2nd Law of Thermodynamics and its necessary and sufficient condition. Since the gravitational potential played an important role, it is also hoped that someone can verify these speculations experimentally.

7) Among the discussed topics: The first is on the solubility of materials, including gases; The second is on the solubility product of a compound, the formulas for the molar chemical potentials of solutes, the required verifications, and the size effect; The third topic is on the molar chemical potential and surface energy of a solid, it is addressed that surface energy is a driving force for spontaneous evolutions like sintering and Ostwald ripening; The fourth topic is to focus on the constraints that should be fulfilled when conducting experiments or establishing formulas related to the Atomistic 2nd Law of Thermodynamics.

Remark: The author believes, the concepts, theories or formulas related to Atomistic 2nd Law of Thermodynamics should comply with the observed phenomena and suitable experimental verifications. This is the major reason why the author is encouraging researchers to verify experimentally the various phenomena related to Atomistic 2nd Law of Thermodynamics.

Conflicts of Interest

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

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