Research Square

Preprints are preliminary reports that have not undergone peer review.
They should not be considered conclusive, used to inform clinical practice,
or referenced by the media as validated information.

On Molecule Symmetry, Latent Heat, and Entropy

Henmei Ni

henmei_ni@seu.edu.cn

School of Chemistry and Chemical Engineering, Southeast University https://orcid.org/0000-0002-3315-8475

Research Article

Keywords: Molecule Symmetry, Latent Heat, Heat Transfer, Superfluid, Phase Transition, Thermodynamics

Posted Date: February 27th, 2026

DOI: https://doi.org/10.21203/rs.3.rs-8975789/v1

License: This work is licensed under a Creative Commons Attribution 4.0 International License.
Read Full License

Additional Declarations: The authors declare no competing interests.

On Molecule Symmetry, Latent Heat, and Entropy

Henmei Ni*

School of Chemistry and Chemical Engineering, Southeast University, Southeast University Rd. 2#, Jiangning, Nanjing 211189, China. *Email: henmei_ni@seu.edu.cn

Abstract

This paper suggested correlating entropy with the geometric symmetry of molecular orbitals rather than with the atomic mass distribution within a molecule. Employing the NIST thermodynamic parameters of substances at saturation, linear regressions of exothermic heat over T give $\varepsilon_{exo} = B - \frac{3+2A}{2}RT$. B is the molar heat of liquefication, which equals the latent heat (ΔH_v^{Φ}) at the boiling point. A reflects the molecule's symmetry; the more symmetric the molecular orbits, the smaller A. For example, the symmetry of inert gas atoms gives the operation number n = 1 in the theoretical frame of the geometric symmetry of atomic mass distribution. However, three p orbitals give n = 7; correspondingly, the A values for Ne, Ar, Kr, and Xe are 2.5518, 2.9104, 2.9140, and 2.9178. Similarly, a tetrahedral C sp^3 gives n = 8, CH_4: A=2.9519. Hence, assuming that $\frac{3+2A}{2}R$ is the lost entropy, $\frac{n-2A}{2}R$ may be regarded as the residual in liquid. According to the above suggestion, CO is more symmetric than CO_2. Moreover, the similarity in A between ethylene and ethane, propylene and propane, etc., implies that the C-C π bond should be rotatable rather than rigid. Helium-4 superfluid finds an increase in entropy as T decreases from 3.5 to 0.8 K. Clausius-Clapeyron equation was derived from ε_{exo}.

Keywords: Molecule Symmetry, Latent Heat, Heat Transfer, Superfluid, Phase Transition, Thermodynamics

Introduction

Molecular symmetry significantly affects the phase transition temperatures (T_m and T_b) and solubility of organic compounds. [1-10] As a general rule [1], crystals of symmetrical molecules have higher melting temperatures but are less soluble than crystals of less symmetrical molecules with similar structures. A prevalent explanation is based on Gibbs free energy at the thermal equilibrium regarding the relationship between the enthalpy (ΔH), entropy (ΔS), and phase transition temperature. A higher temperature implies a smaller ΔS because enthalpy is usually related to molecular interactions, such as ionic, polar, and hydrogen-bond interactions. Isomers have the same functional groups; thus, the enthalpy should be equal. Hence, entropy dominates the difference in phase transition temperatures between isomers. Walden showed that the average entropy of melting for many "coal tar" derivatives, which consist mainly of aromatic hydrocarbons, is constant, 13.5 cal/(deg·mol) [8]. In contrast, for

small spherical molecules, it is 3 cal/(deg·mol) [9]. The boiling entropy of non-hydrogen-bonding organic compounds generally follows Trouton's rule, 88 J/(deg·mol) [10]-[12]. However, conventional thermodynamics infers that molecules have a large degree of rotational and conformational freedom in both the liquid and the gas; the entropy associated with changes in these parameters upon boiling is small. Conversely, liquid molecules gain tremendous translational freedom upon entering the gas phase. The entropy of boiling is almost entirely the result of this increase in translational motion. In contrast, the entropy of melting is primarily due to rotational and conformational factors and only slightly due to translational factors. Therefore, the factor of molecular symmetry gradually fades in the studies of boiling entropy. Instead, Joback quantified the contributions of functional groups to enthalpy to predict boiling points and solubilities. [13] After that, this method dominated studies of boiling points. [14]-[17]

The intimate connection between molecular symmetry and melting temperature is quantified by Yalkowsky et al. [18]. A high melting enthalpy implies strong bonding. Molecular symmetry may contribute to tighter crystal packing via shape-cohesion effects. The molecular rotational symmetry number (σ) is introduced to express the impact of molecular symmetry on the entropy of melting: the number of indistinguishable positions that can be obtained by rigidly rotating the molecule about its center of mass. The greater the molecular rotational symmetry number, the higher the probability of the molecule being in the correct orientation. In the solid phase, the symmetry of a molecule results in a residual amount of molar entropy of magnitude $Rln\sigma$ above that of a similar but non-symmetrical molecule. Consequently, the difference in entropy between the liquid and solid phases will be negligible for the more symmetrical molecule. This, in turn, means that symmetry in a molecule reduces the entropy gained upon melting for that compound (ΔS_m). Either of the two effects listed above, not to mention a combination of the two, would result in a higher melting temperature for a symmetrical molecule over a non-symmetrical one.

$$\Delta S_m = 56.5 - Rln\sigma \quad (\text{J K}^{-1}\text{mol}^{-1}) \qquad (1)$$

The significant intuitive appeal of the above explanation comes from its conceptual and numerical arguments being valid and entirely consistent. However, the same account fails to explain a widespread observation: Symmetrical molecules, which, as a general rule, do have higher melting temperatures, quite often have greater melting entropies than their less symmetrical isomers. Therefore, Gilbert introduced the "entropy-enthalpy compensation" effect into Eq. 1, namely that ΔS_m is dependent upon the enthalpy of melting ΔH_m. [19] `Flexible' molecules (potentially multi-conformational) tend to yield higher values of $\Delta S_m$ for a given $\Delta H_m$ than `rigid' ones.

Another effort to incorporate molecular symmetry into the phase transition temperature is to maintain theoretical consistency. [2], [20]-[22] Within a homologous series, adding a substituent that increases internal cohesive forces also increases densities, boiling points, heat of vaporization, refractive indexes, and surface tensions. However, the melting points are the outstanding exceptions, which behave idiosyncratically. The lack of molecular symmetry in the functional group contribution equations is considered a reason.

Although significant progress has been made in predicting the physical properties of organic compounds, some fundamental problems still exist. First, it is hard to correlate the contributions of functional groups and molecular symmetry numbers with thermodynamic properties such as pressure and temperature. For example, the Clausius-Clapeyron equation indicates that pressure affects the phase transition temperatures. [23] Second, determining the functional group contribution and symmetry number is arbitrary. For example, the symmetry number of CH_4 is designated as 12 because it has 4 C_3 rotational axes. [18] However, nine symmetry operations should be degenerate in the energy level.

Moreover, the symmetry number of a monoatomic gas is designated as 200. [18] In contrast, the symmetry number of entirely asymmetrical molecules CHXYZ (X, Y, and Z denote different atoms or groups except for H) is 1. It is beyond common sense that the spin of an atom can contribute so much entropy. Moreover, it seems to be the inverse of entropy, reflecting the diversity of molecular configurations. Third, the geometric symmetry of the mass distribution is selected solely without any reasoning. However, in quantum theory, the symmetry of orbits is vital to the reactions [24], [25] and spectroscopy [26], [27]. Therefore, it is essential to assess the definition of molecular symmetry and the quantifying approach based on the principles of straightforwardness and reasonableness.

In our previous papers [28]-[32], we defined heat in terms of the first law of thermodynamics. In classical thermodynamics, only the variation of internal energy is considered, instead of the variation of total energy in a thermodynamic system, while the variations in kinetic and potential energy are neglected without any convincing reason. In the new thermodynamics, variations in kinetic and potential energy are also considered, thereby defining heat. Based on the definition of heat, a series of achievements were obtained, such as the state equation of real gas [28], gas solubility and gas-liquid interfacial tension [29], the specific heat capacity of real gas [30], the equilibrium distance of molecular interaction [31], and the state equation at isotherm [32]. Therefore, this paper will address molecular symmetry and entropy.

Results and discussion

First, it should be noted that, unless otherwise noted, all thermodynamic parameters of the substances used in the calculations, i.e., T, P, V_G, and V_L, are cited from the NIST Chemistry WebBook, and are the experimental data.

Scaling the Symmetry of a Molecule

The exothermic heat at saturation is defined as [31],

$$-\frac{\varepsilon_{exo}}{RT}=\frac{3}{2}+ln\frac{V_L}{V_G}-\frac{\pi^{\alpha}mg}{RTV_G} \qquad (2)$$

Thus,

$$Y=-\frac{\varepsilon_{exo}}{RT}-\frac{3}{2}=ln\frac{V_L}{V_G}-\frac{\pi^{\alpha}mg}{RTV_G} \qquad (3)$$

As shown in Fig. 1, a linear regression perfectly fits the curve of $Y\sim\frac{1}{T}$ with a coefficient of determination R^2=1 from M.P. to the critical temperature (T_c). Here, note that the maximum value of R^2 is 1. R^2=1 indicates that the fitting is perfect. As R^2 deviates from 1, the worse the fit. Since the coefficient R in the figures duplicates the gas constant, D^2 will be used instead of R^2 in the context. Therefore, Eq. 2 may be altered by Eq. 4.

$$-\frac{\varepsilon_{exo}}{RT}=\frac{3+2A}{2}-\frac{B}{T} \qquad (4)$$

A is the intercept, a dimensionless value, and B is the slope with the Kelvin temperature. Helium is an exception, which will be discussed in the last section.

Inspired by the inert gases, all other gases are treated using the thermodynamic data issued by NIST. The fitting results of some representative examples are shown in Fig. 2.

As shown in Fig. 2, Eq. 4 is universal, irrespective of the molecules' properties. Moreover, the following results are obtained by comparing A, B, and D^2.

1) The effects of atomic/molecular mass and molecular interactions on the A and D^2 values are not observed; however, they are significant on the B value. The series of inert gases in Fig. 1 exemplifies the mass impact. B values of NF_3 and NH_3 in Fig. 2 exhibit the effects of molecular interactions.

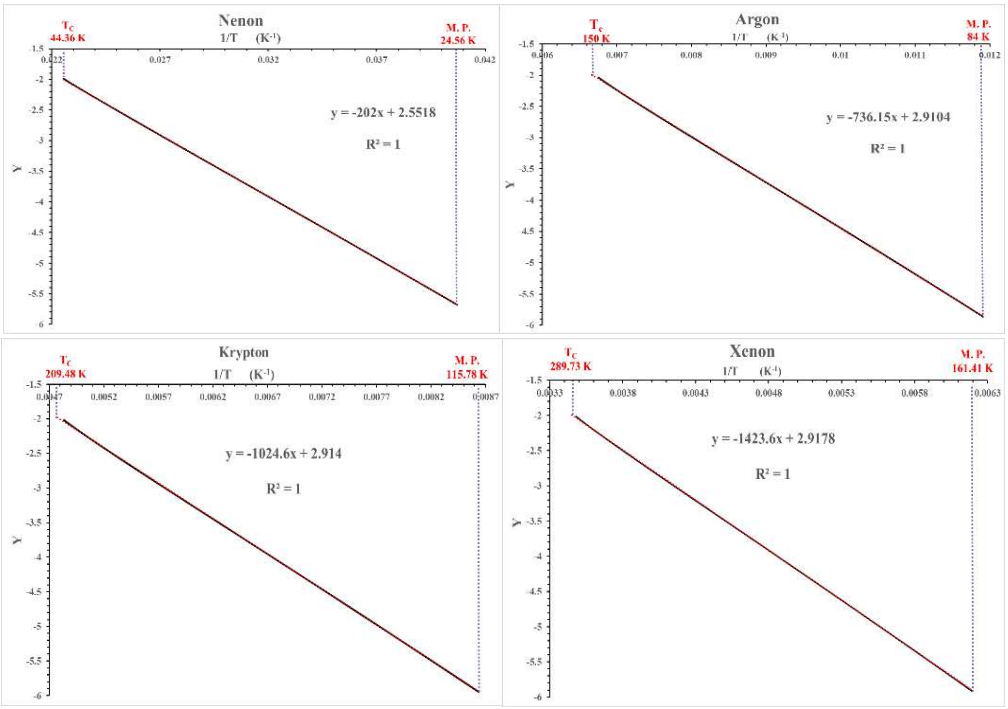


Figure 1, $Y \sim \frac{1}{T}$ of inert gases

2) A and D^2 significantly correlate with molecular symmetry. A symmetric molecule gives a much smaller A, and in most cases, D^2=1 or 0.9999, whereas an asymmetric molecule gives an inverse. For example, cyclopropane is symmetric; thus, A=3.7396, D^2=1. In contrast, propane is asymmetric; therefore, A=5.0709, D^2=0.9974. As a result, A and D^2 may be the criteria for assessing the molecule's symmetry.
3) As shown in Fig. 2, in the cases of smaller D^2, e.g., NF_3: D^2=0.999, the linear regression can proceed in different temperature intervals to gain $D^2 \rightarrow 1$ as much as possible. It is natural and rational because, for asymmetric molecules, the molecular packing in a liquid may be affected by temperature. For example, as the temperature increases from M.P. to T_c, NF3: A decreases from 5.7103 to 3.6213, while B (absolute value) decreases from 1566.7 to 1317.8 K. Since A and B represent the difference of packing status between gas and liquid, the more significant value indicates that the packing is tighter in liquid, provided that the packing status in gas is entirely random. Hence, as molecular motion slows at lower temperatures, it is reasonable that the packing becomes tighter, thereby yielding larger values of A and B. This result indicates that A and B vary with temperature. The linear regression over the entire temperature range from M.P. to T_c yields the average A and B values. D^2=1 is just a signal of tiny variation.
4) The same configuration exhibits a different symmetry according to A and D^2. For example, the configuration of both NH_3 and NF_3 is a tetrahedron with a vertex occupied by an unbonded p orbital. However, the averaged A and D^2 of the two molecules are quite different. D^2=0.9998

exhibits that NH_3 is close to a symmetric molecule, while D^2=0.999 indicates that the symmetry of NF_3 is inferior. However, an inverse conclusion is drawn from the A values (NH_3: A=4.8459; NF_3: A=4.1011). Therefore, we must use the interval value. In the 85-97.5K interval, the linear regression of NF_3 yields A=5.7103. Comprehensively, it is concluded that the symmetry of NH_3 is superior to that of NF_3. Fortunately, the assessment is consistent across pairs of H_2O/H_2S and CH_4/CF_4. For H_2O, A=5.3322, D^2= 0.9998; H_2S: A=3.6898, D^2= 0.9999, whilst for CH_4, A=2.9519, D^2=1; CF_4: A=4.0262, D^2= 0.9997. Accordingly, the symmetry of H_2S and CH_4 is better than that of their counterparts. It indicates that the unbonded p orbital, e.g., 2p of the Fluorine atom, and its size, e.g., 3p of the Sulfur atom, impact the molecule's symmetry. This result suggests that the symmetry of the molecular orbital, rather than the conventional mass symmetry [18], is proper to be a criterion for assessing molecule symmetry. However, the sign symmetry of the molecular orbital in Woodward and Hoffmann's rule [25] should be excluded. As a result, set $D^2 \rightarrow 1$ as possible, A is solid for assessing the molecule's symmetry, though, in most cases, the averaged A is reliable enough.

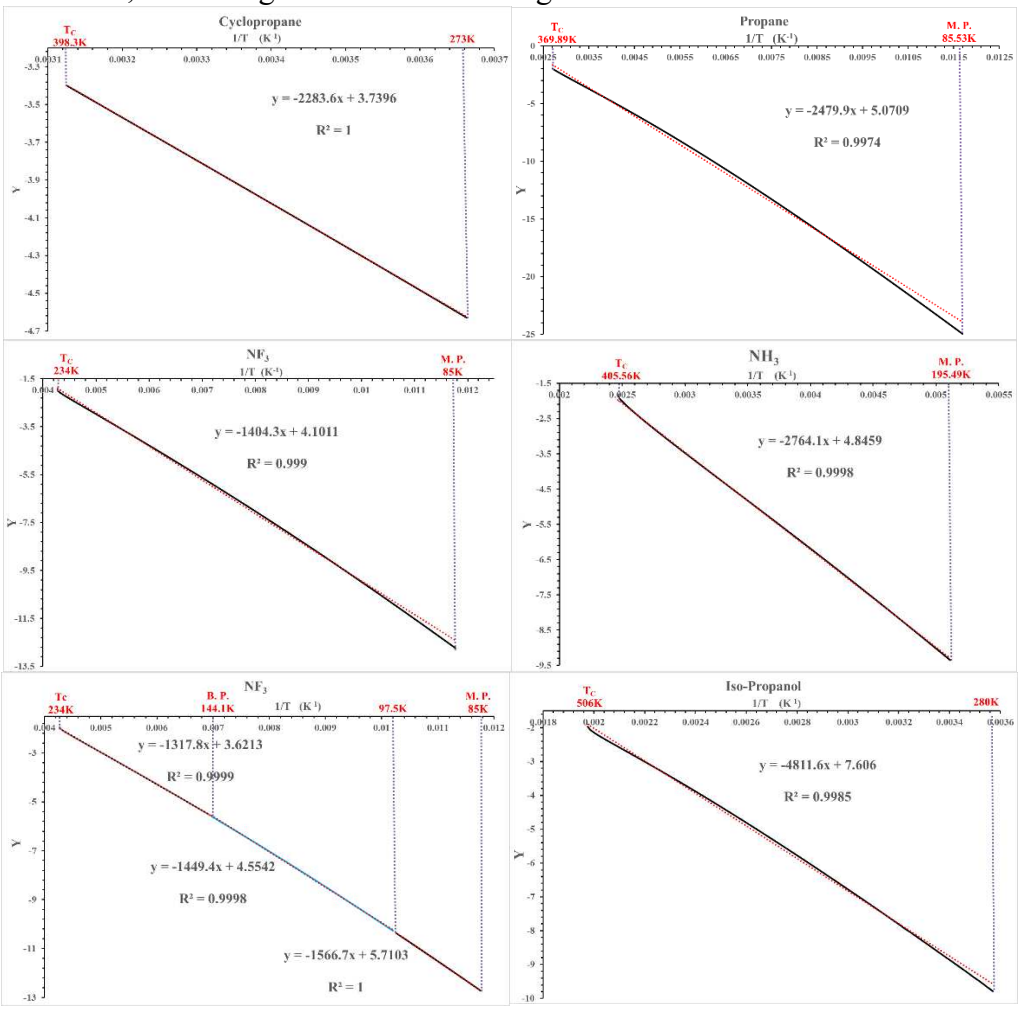


Figure 2, Curves of $Y \sim 1/T$ and the results of linear regression of some representative gases

Figure 3 summarizes the average A values of small molecules. It is striking that some asymmetric molecules, e.g., CO, exhibit greater symmetry than symmetric molecules, for instance, CO_2, according to the theory of mass symmetry. It supports the molecular orbital symmetry argument. Fig. 4 shows the average A values of hydrocarbon molecules. Four linear relationships are observed. For example,

except for CH_4, the straight-chain alkanes with an even number of carbons and those with an odd number of carbons lie on straight lines. It reflects the better symmetry of alkanes with an even number of carbons. However, cyclo-C_4F_8 does not fall on the line composed of CH_4, cyclopropane, etc. Considering the higher A values of fully fluorinated alkanes, it indicates that the effects of the unbonded *p* orbitals of Fluorine are significant. A striking observation is that the *A* value of propene equals that of propane, while the spot of benzene overlaps that of cyclohexane. It is beyond the anticipation provoked by the symmetry of a double bond.

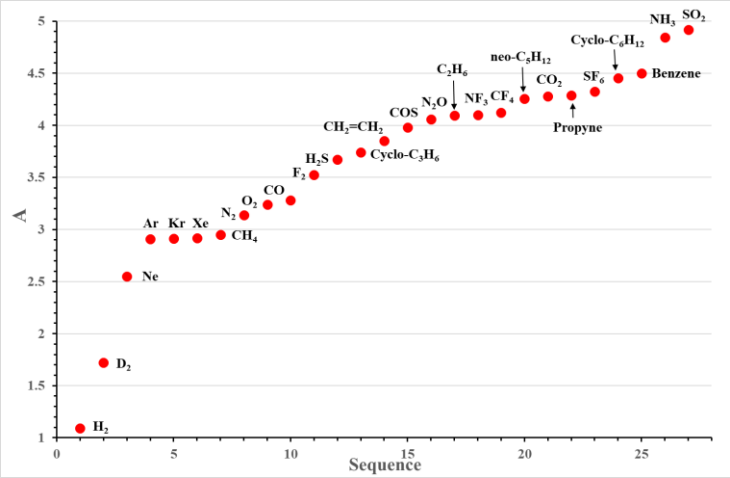


Figure 3, Averaged *A* values of various small molecules.

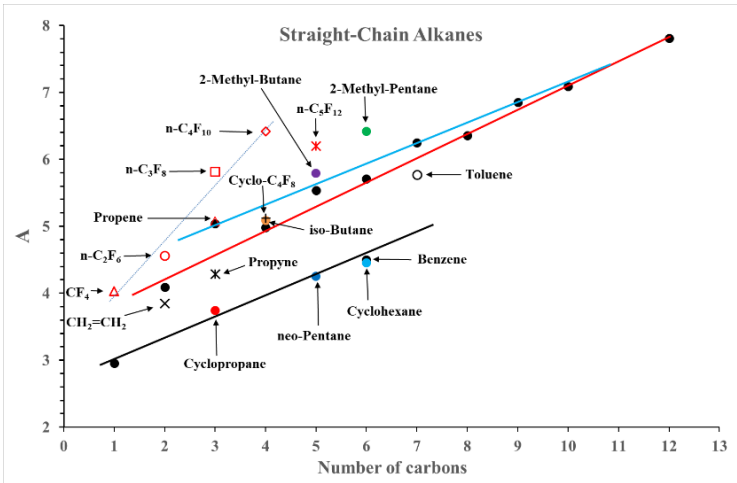


Figure 4, *A* values of (fluorinated) hydrocarbons
(solid black cycles denote straight-chain alkanes)

Fig. 5 exhibits the *A* values of fluorinated hydrocarbons and alcohols. Adding fluorine atoms to alkanes reduces symmetry due to the three unhybridized *p* orbitals. Therefore, the fully fluorinated alkanes are less symmetric than their counterparts. Alcohols show higher *A* values that are equivalent to those of decane and dodecane (Fig 4). This is unusual.

Now, it is clear that *A* and D^2 are tightly related to the molecule's symmetry.

Provided that $\frac{3+2A}{2}R$ is the entropy change of evaporation (ΔS_v), *A* must be an item reflecting the entropic contribution of symmetry operations because the item of long-distance kinetic energy is

set to 3/2. Moreover, the conventional mass symmetry is not suitable for describing the variations of A and D^2. Therefore, the shapes of atomic/molecular orbitals are worthy of discussion.

Given that the description of the quantum theory is correct, for instance, the outer atomic orbital of inert gas (excluding He) at the ground state is s^2p^6, and the p orbital shields the s orbital. Fig. 6 exhibits the shape of atomic/molecular orbits and the number of symmetry operations.

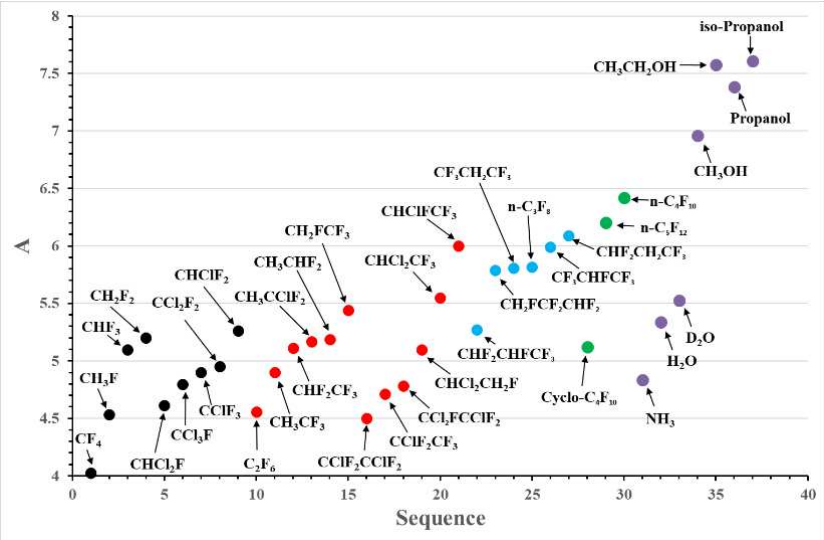


Figure 5, A values of fluorinated hydrocarbons and alcohols

As shown in Fig. 6, using Argon as an example of inert gases, the operation number, n, of p^6 atomic orbital is 6+1 (1 denotes E operation). Assuming that each operation contributes 1/2 RT to either the rotational kinetic energy or the entropy of the ensemble, $n/2$=3.5 is close to the A value of Ar, 2.9104. This means that 0.5896 RT remains in the liquid, assuming that a molecule in the gas phase is entirely free and has all the operational numbers. It converts to rotational and translational energy in the liquid state, even though most operations are restricted by the dense packing of molecules. Similarly, for Ne, Kr, and Xe, the values of $n/2$-A are 0.9492, 0.5896, 0.586, and 0.5822, respectively. It implies that the smaller the atom, the more energy remains. In other words, the larger the atom, the tighter the packing in the liquid. It is consistent with the density variation.

CH_4 has a similar A value, 2.9519. Yalkowsky [18] designated 3 to $1C_3$. Accordingly, CH_4 owns 12 operation numbers. However, $1C_3$ is considered a degenerate energy state in this paper. Hence, as shown in Fig. 6, n of CH_4 is 8 ($4C_3$+$3C_2$+E); thus, it remains 1.0481 in liquid.

As we try to correlate the number of symmetry operations to A, it should be emphasized that a default prerequisite is $n/2 > A$. Otherwise, $RT/2$ of each operation must be adjusted case by case to fit A. Although the choice is arbitrary, we choose the former, namely that $n/2>A$, as the prerequisite for the following discussion.

As shown in Fig. 6, in contrast to the concept of mass symmetry, N_2 (A=3.1403, D^2=0.9999) is more symmetric in comparison with O_2 (A=3.2418, D^2=0.9994) and F_2 (A=3.5235, D^2=0.9994). In addition, CO (A=3.2879, D^2=0.9999) is also symmetric.

For N_2, n=6, i.e. $1C_4$+$4C_2$+E, but A=3.1403. Therefore, an additional symmetry operation should be found. Conventionally, two π bonds are considered rigid. However, the σ bond's rotation must be included to ensure $n/2>A$. A σ bond rotation supplies two operations: a cross of p orbitals of two N atoms and a C_2 of cross. Hence, n = 8 for N_2. The twist of two π bonds is also acceptable, but we must endow a twist operation with RT. Compared with a σ bond rotation, a σ bond rotation is a better choice,

as it is universal across other molecules. As mentioned above (Fig. 4), the C-C π bond in the ethylene and benzene rings does not exhibit symmetric superiority compared to ethane and cyclohexane. Hence, if the σ bond in ethylene and benzene could rotate freely as in ethane and cyclohexane, the similar A values could be rationally interpreted. Moreover, CO_2 (A=4.2768, D^2=1) should have more than nine symmetry operations. Only two σ-bond rotations can supply so many symmetry operations. Those analyses are consistent with the oscillating structure of the π bond, namely that two bonded electrons may immigrate to one of the bonded atoms. [31]

CO is similar to N_2 because a spare O p^2 orbital can form a π bond with a vacant C p^0. Therefore, n=8, satisfying A=3.2879. Similarly, for CO_2, moving one pair of spare O $2p$ electrons from C to O increases the number of operations.

For O_2, as shown in Fig. 6, n=6. However, Fig. 7 shows that the maximum A = 4.2336 occurs for n $\geqslant$ 9. O_2 has two spare O p^2 orbitals. Since the kinetic energies of all electrons are equal, apart from a σ bond, the molecular structure oscillates O p^4 ↔ O p^2, by which an additional 5 operations are obtained. Therefore, n=11 for O_2.

F_2 has four spare p^2 orbitals. As shown in Fig. 6, n=11. It satisfies the maximum A=4.4655 corresponding to $n \geq 9$ (Fig. 7).

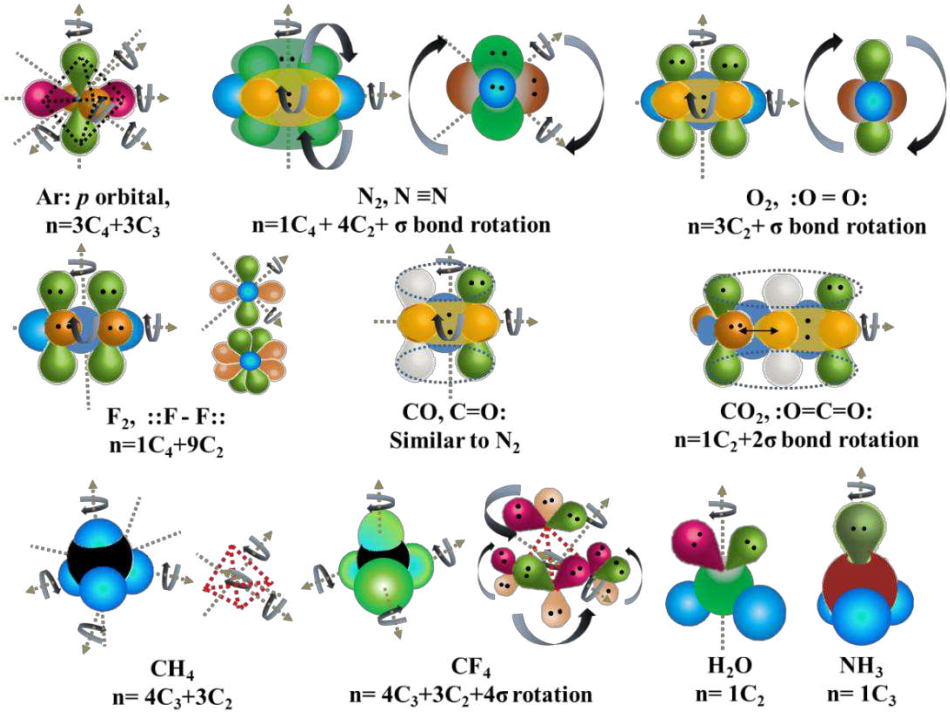


Figure 6, Orbital symmetry of some molecules

As shown in Fig. 7, H_2O and H_2S are asymmetric molecules in terms of the geometric symmetry of mass. However, H_2S acts as a symmetric molecule. A=3.6898 corresponds to $n \geq 8$. It is likely ascribed to the large $3sp^3$ hybridized orbital of S, relative to the small $1s$ orbital of H. Two H-S bonds do not destroy the tetrahedral symmetry of the sp^3 hybridized orbital (see CH_4, n=8), though it inevitably deforms. Hence, n=8 is possible.

In contrast, H_2O in ice is abnormal [33]. A breakpoint is found at M.P. due to the abrupt decrease of density, and A=9.2823 corresponds to n≥19 below M.P. It is hard to get so many symmetry operations from H_2O in gas. Meanwhile, such a large A (>9) is only found in the longer alkanes (C >

4) near M.P. Moreover, it is rare even in alcohols, i.e., methanol, ethanol, propanol, and isopropanol. Therefore, two causes are possible. The first is that migrating two hydrogen atoms among the four vertices of an O sp^3 tetrahedron increases the operation number. The second is that the complex forms due to the strong H-bonds at temperatures below M. P.

Like H_2S, NH_3 appears to be a symmetric molecule with A=4.832 and D^2=0.9999. This implies that the volume of N $2sp^3$ hybridized orbitals is much larger than that of the H1s orbital; thus, the tetrahedral symmetry remains major. However, even though a tetrahedron gives n=8, it doesn't satisfy A. Hence, considering the packing of molecules, the immigration of H among the four vortexes of a tetrahedron is a kind of freedom, provided that immigration is forbidden in liquid because another NH_3 occupies the vacant orbital via the hydrogen bond. By this means, n=11 is obtained for NH_3. Such an approach is also suitable for H_2O. From M.P. to B.P. of H_2O, A=5.9334 corresponds to $n\geq12$, while above B.P., A=5.1168. As shown in Fig. 6, because H_2O has two spare sp^3 hybridized orbitals, two H atoms can migrate between them. It produces 6 additional operations. Therefore, $n = 14$ for H_2O.

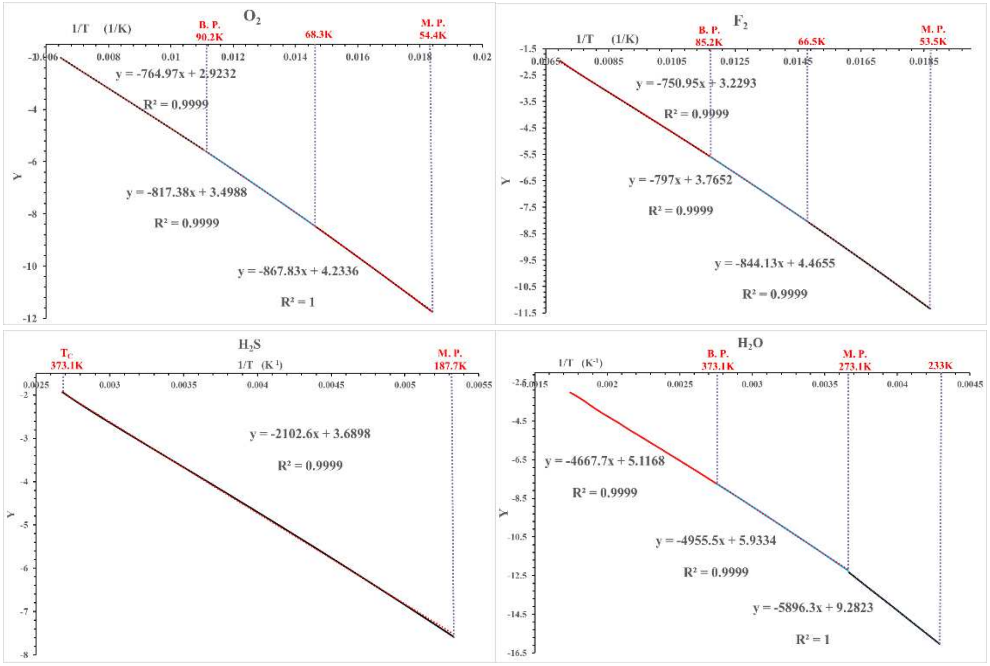


Figure 7, Y via reciprocal T of some asymmetric molecules

However, NF_3 (A=4.1011, D^2=0.999) exhibits asymmetry due to the unbonded three occupied F sp^3 hybridized orbitals. As shown in Fig. 3, near M.P., A=5.7103 corresponds to $n\geq12$. The tetrahedron possibly collapses. Therefore, the symmetry operations should be a molecule C_3, with three migrations and a contribution from the rotation of three F sp^3 hybridized orbitals. Since each F atom has a C_3, the total operations should be 9, i.e., molecule C_3×F atom C_3. Subtracting a C_3, n=13 for NF_3.

Due to the application of molecular orbitals, CF_4 exhibits a symmetry different from CH_4. As shown in Fig. 6, n=8 for a tetrahedron, in addition to 4 rotations of σ bond, thus n= 4 molecule C_3×4 F C_3 -4 molecule C_3 + 3 molecule C_2×4 F C_3- 3 molecule C_2 = 22, namely that CF_4 has 22 operations, n=22. However, since a fluorine atom is bigger than a carbon atom, in addition to the three big sp^3 orbitals of each fluorine atom, the rotation of the σ bond may be restricted. Something like the synergistic rotation may exist. It may reduce the number of operations by half. Hence, CF_4 gives A=4.6377 near M.P., corresponding to n=10. In contrast, SF_6 exhibits excellent symmetry with A=4.2976 and D^2=0.9999, corresponding to $n \geq 9$. In the theory of mass symmetry, it is an octahedron

consisting of 8 equilateral triangles formed by the d^2sp^3 hybridized orbitals of a sulfur atom. However, according to the theory of this paper, the optimal structure is a regular tetradecahedron with three vertices occupied by vacant *d* orbitals. Accordingly, it is hard to scale the symmetry.

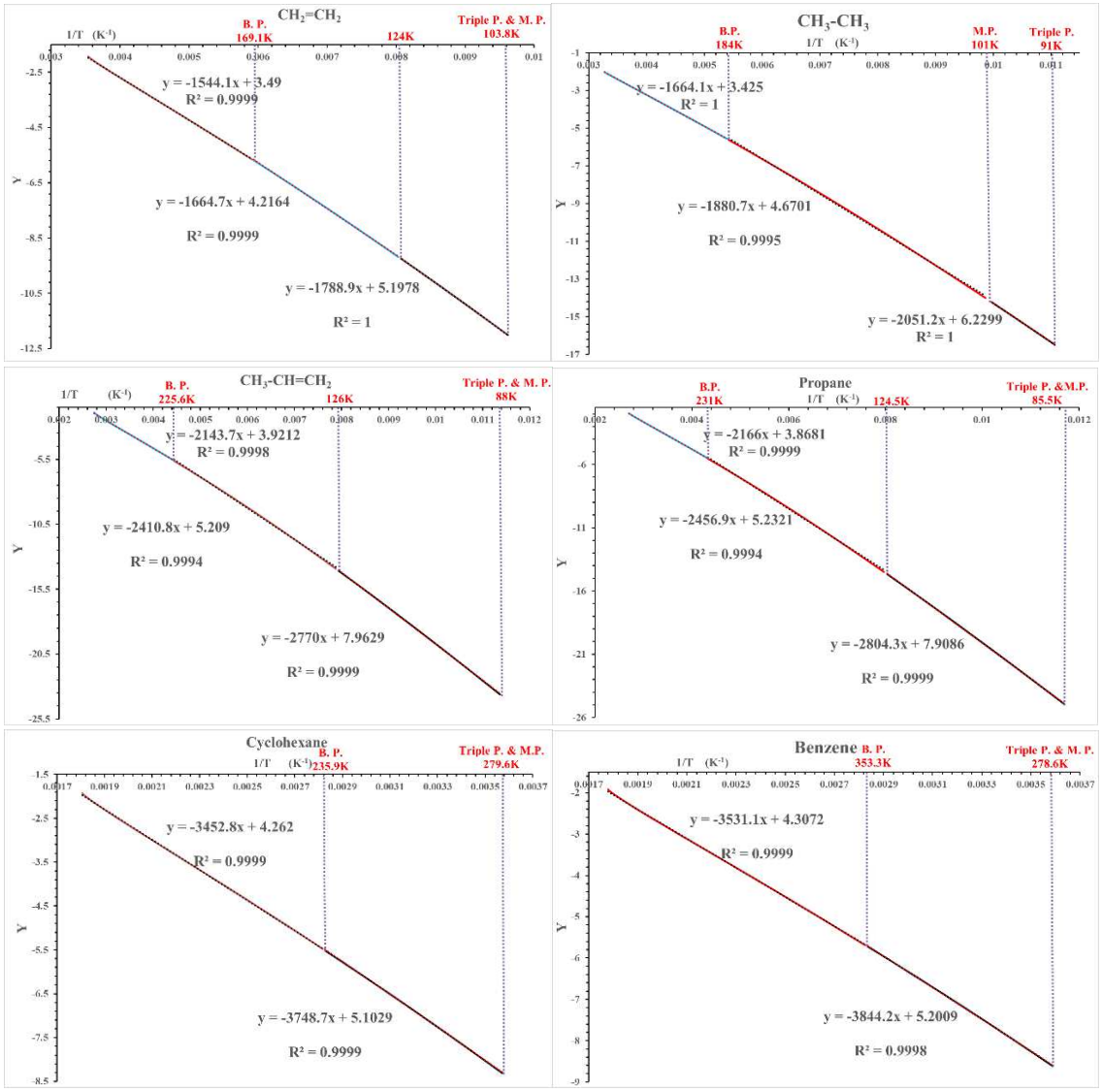


Figure 8, $Y \sim 1/T$ of cyclohexane and benzene

As shown in Fig. 4, the similarities between ethylene and ethane, propane and propene, and cyclohexane and benzene in the *A* values align with common knowledge of molecular structure. Unlike the rotatable σ bond, a C-C π bond is usually recognized as a rigid and symmetric bond; thereby, as an example, benzene should have exhibited excellent symmetry relative to cyclohexane. However, as shown in Fig. 8, the difference in the *A* values is not as significant as anticipated. A cyclohexane molecule is commonly recognized as a soft regular-hexagon frame that the conformations of chair type and boat type can form due to the rotation of C-C σ bonds. In contrast, a benzene molecule is a rigid, regular-hexagonal pie fixed by a grand π bond. Therefore, the operation number of a benzene ring can be readily determined, i.e., n = 12 ($1C_2$+$3C_3$+$1C_6$+$6C_2$+E). Correspondingly, above B.P., A=4.3072 corresponds to n=9, while below B.P., A=5.2 corresponds to n=11. However, for cyclohexane, the max. n = 7 (3 boat types×1 C_2 + 3 chair types×1C_2 +E). It needs additional symmetry operations. Based on effective packing and entropy, the mirror operation can be added to cyclohexane operations, provided

it does not overlap with the rotation operation. By this means, n=3 boat types × (1 C_2 + 1 σ^2) + 3 chair types × (1C_2 +1 σ^2) +E =13. Unfortunately, such a treatment is not suitable for ethylene. Therefore, as mentioned above, for N_2, etc., π bonds must be rotatable to satisfy $n/2 \geq A$. There are only 3 C_2 operations for CH_2=CH_2, but the max is A=5.1978, corresponding to n≥11. In contrast, ethane has the operations, 3C_3+9C_2+3C_2+E=16, thus the max. A=6.2299 is proper.

However, as the chain extends, maintaining the scaling symmetry becomes increasingly difficult.

As shown in Fig. 5, alcohols have a large average A, generally >7. Near their M.P., A=8.1776, 9.0645, 8.7631, and 8.8537 correspond to methanol, ethanol, n-propanol, and isopropanol. For those molecules, symmetry is out of the question. It is too complicated. The diversity of conformations or the number of freedoms should concern the molecules' packing and entropy.

In summary, the first attempt to connect the entropy of a phase transition with the symmetry of atomic/molecular orbitals is successful. Compared with the mass distribution theorem, [18] this method is operable with rational results. For example, the symmetry of inert gas atoms gives the operation number n = 1 in the theoretical frame of the geometric symmetry of atomic mass distribution. Meanwhile, for an asymmetric molecule CHXYZ where X, Y, and Z are different atoms, the operation number is also n = 1. Hence, it is not distinguishable by symmetry. However, based on the shape and size of molecular orbitals, the symmetries of the above two molecules are distinguishable with different rational A values.

Latent Heat

The following tables list the A and B values of some substances.

Table 1, A and B values of small molecules

Gas	A	B (K)	A+3/2	T_c* (K)	T_c (K)	R×B (kJ/mol)	Latent Heat (kJ/mol)
He	-0.405	9.5516	1.095	8.72	5.2	0.079	0.084(4.15K) [34]
H_2	1.0916	105.48	2.5916	40.7	33.15	0.88	0.90(21.15K) [34]
D_2	1.7213	144.46	3.2213	44.85	38.34	1.20	-
Ne	2.5518	202.0	4.0518	49.85	44.36	1.68	1.71(27.15K)
Ar	2.9104	736.15	4.4104	167.21	156.66	6.12	6.53 (87.15K) [34]
Kr	2.914	1024.6	4.414	233.24	209.48	8.52	9.03(121.2K)
Xe	2.9178	1423.6	4.4178	322.04	289.73	11.84	12.6(165.2K) [34]
N_2	3.1403	646.79	4.6322	139.63	126.19	5.38	5.58 (77.15K) [34]
O_2	3.2418	802.48	4.7418	169.23	154.58	6.67	6.82(90.15K) [34]
CO	3.2829	698.16	4.7829	145.97	132.85	5.80	6.0 (81K)
F_2	3.5235	783.58	5.0235	155.98	144.41	6.51	6.32(85.15K) [34]
H_2S	3.6713	2097.6	5.1713	405.62	373.1	17.44	18.6 (243K)
COS	3.9798	2221	5.4798	405.31	378.77	18.47	18.3 (299K)
N_2O	4.0568	1861.8	5.5568	335.08	309.52	15.48	16.5 (184.7K)
NF_3	4.1011	1404.3	5.6011	250.72	234	11.68	11.59
CF_4	4.1222	1382.0	5.6222	245.81	227.51	11.49	12.1 (212K)
CO_2	4.2768	1906.7	5.7793	330.06	304.09	15.85	16.7 (288K)
SF_6	4.3239	2000.3	5.8239	343.46	318.73	16.63	-
NH_3	4.8459	2764.1	6.3459	435.57	405.56	22.98	22.7 (308K)

SO_2	4.9188	2940.1	6.4188	458.05	430.64	24.44	24.9 (263K)

Note: the temperature in the parenthesis is B.P.

Table 2, *A* and *B* values of alkanes

Gas	A	B (K)	A+3/2	T_c* (K)	T_c (K)	R×B (kJ/mol)	Latent Heat (kJ/mol)
CH_4	2.9519	943.95	4.4519	212.03	190.56	7.85	8.17 (111.7K)
C_2H_6	4.0933	1815	5.5933	324.50	305.32	15.09	14.7 (194.1K)
n-C_3H_8	5.0709	2479.9	6.5709	377.41	369.89	20.62	19.04 (231.1K)
Cyclo-C_3H_6	3.7396	2283.6	5.2396	435.83	398.3	19.00	20.0 (240.3K)
n-C_4H_{10}	4.9811	2873.3	6.4811	443.34	425.13	23.89	22.4 (272.7K)
i-C_4H_{10}	5.0867	2774.3	6.5867	421.20	407.81	23.07	21.3 (261.3K)
n-C_5H_{12}	5.5374	3405.8	7.0374	483.96	469.8	28.32	25.79 (309.2K)
2-Me-C_4H_{11}	5.7903	3386.4	7.2903	505.66	461.35	30.65	24.69 (301K)
n-C_6H_{14}	5.7066	3797.2	7.2066	526.91	507.6	31.56	28.85 (341.9K)
neo-C_5H_{12}	4.2544	2690.9	5.7544	467.62	433.74	22.37	23.1 (397K)
Cyclo-C_6H_{12}	4.4558	3541.2	5.9558	594.58	553.6	29.44	29.97 (353.9K)
2-Me-C_5H_{13}	6.4178	3927.9	7.9178	496.08	497.8	32.66	27.79 (333.4K)
n-C_7H_{16}	6.2496	4301.7	7.7496	555.09	540.2	35.76	31.77 (371.6K)
n-C_8H_{18}	6.3553	4628.6	7.8553	589.23	568.9	38.48	34.41 (398.8)
n-C_9H_{20}	6.8522	5102.9	8.3522	610.96	594.55	42.43	36.91 (424K)
n-$C_{10}H_{22}$	7.0868	5453.3	8.5868	635.08	617.8	45.34	38.75 (447.3K)
n-$C_{12}H_{26}$	7.8104	6259.6	9.3104	672.32	658.2	50.42	51.6 (415K)

Note: the temperature in the parentheses is B.P.

Table 3, *A* and *B* values of unsaturated hydrocarbon

Gas	A	B (K)	A+3/2	T_c* (K)	T_c (K)	R×B (kJ/mol)	Latent Heat (kJ/mol)
CH_2=CH_2	3.8512	1622.3	5.3512	303.17	282.35	13.49	13.54 (169.4K)
CH_3-CH=CH_2	5.037	2430.7	6.5037	373.74	365.21	20.21	18.42 (225.5K)
CH_3-C≡CH	4.2869	2521.1	5.7869	435.66	402.38	20.96	21.9 (374K)
Benzene	4.5019	3620.7	6.0019	603.26	562.02	30.10	30.77 (353.25K)
Toluene	5.7686	4406	7.2686	606.17	593.2	36.63	33.18 (383.8K)

Note: the temperature in the parentheses is B.P.

Table 4, *A* and *B* values of hydrogen-bonded compounds

Gas	A	B (K)	A+3/2	T_c* (K)	T_c (K)	R×B (kJ/mol)	Latent Heat (kJ/mol)
H_2O	5.3322	4771.2	6.8322	696.45	647.10	39.67	40.68 (373.15K)
D_2O	5.5269	4859.4	7.0269	691.54	643.85	40.40	40.657 (374.57K)
CH_3OH	6.9586	4540.9	8.4586	536.84	513.1	37.75	37.49 (337.7K)
C_2H_5OH	7.5734	4853.2	9.0734	534.86	514.7	40.35	38.8 (351.5K)
n-C_3H_7OH	7.3825	4946.3	8.8825	556.86	536.9	41.12	41.44 (370.3K)
i-C_3H_7OH	7.6060	4811.6	9.1606	525.25	509.4	40.00	39.85 (355.4K)

NH_3	4.836	2761.6	6.336	435.57	405.4	22.96	23.5 (239.0K)

Note: the temperature in the parentheses is B.P.

As shown in the above tables, if defining $T_C^* = \frac{B}{\frac{3+2A}{2}}$, Eq. 4 transforms into

$$-\frac{\varepsilon_{exo}}{RT} = \frac{3+2A}{2}\left(1 - \frac{T_c^*}{T}\right) \qquad (5)$$

In our previous paper [29], it was pointed out that T_c is the temperature corresponding to x_2 = 60~70%, a maximum value that a gas system enables to keep the thermal equilibrium by the heat exchange cycle. Here, T_c^* is the theoretical temperature at $x_2 = 1$. It corresponds to P_c* [32].

Moreover, $\frac{B}{T} = \frac{R \cdot B}{RT}$, as shown in the above tables, $R \cdot B$ equals the latent heat ($\Delta H_v^{\emptyset}$) at B.P. However, in this paper, $R \cdot B$ is the heat delivered by, theoretically, complete liquefaction of 1 mole of gas.

$$-\frac{\varepsilon_{exo}}{RT} = \frac{3+2A}{2} - \frac{\Delta H_v^{\emptyset}}{RT} \qquad (6)$$

Thus,

$$\Delta H_v^{\emptyset} = \frac{3+2A}{2} RT_c^* \qquad (7)$$

Analogous to Gibbs potential, Eq. 6 may be written as, by including the symmetric entropy.

$$\varepsilon_{exo} = \Delta H_v^{\emptyset} - \frac{3+2A}{2} RT = \Delta H_v^{\emptyset} - T\Delta S \qquad (8)$$

Eq. 8 can never be zero unless T=T_c*. It is similar to the definition of internal energy in conventional thermodynamics.

As discussed above, for a symmetric molecule, $H_v^{\emptyset}$ is constant, irrespective of temperature and pressure. However, for an asymmetric molecule, B is different due to the different packing status of molecules in the liquid at various temperatures. Hence, $\Delta H_v^{\emptyset}$ is variable. However, the variation is generally slight except for water below M.P. For example, in Fig. 8 of oxygen, $\Delta H_v^{\emptyset} = 7.22$ kJ/mol near M.P., while $\Delta H_v^{\emptyset} = 6.35$ kJ/mol above B.P. The discrepancy is about 0.87 kJ/mol. The lower temperature gives the higher $\Delta H_v^{\emptyset}$. It is consistent with the experimental results.

Since,

$$lnx_2 = \frac{3+2A}{2} - \frac{\Delta H_v^{\emptyset}}{RT} \qquad (9)$$

Reminiscent of the pressure at saturation, [32]

$$lnP - lnP_c^* = lnx_2 \qquad (10)$$

Thus, provided that A and $\Delta H_v^{\emptyset}$ are independent to the temperature,

$$\frac{\partial lnP}{\partial lnT} = \frac{\Delta H_v^{\emptyset}}{RT} \qquad (11)$$

Eq. 11 deforms into the Clausius-Clapeyron equation. Of course, it is an approximation because A and $\Delta H_v^{\emptyset}$ are, to some extent, dependent on the state parameters.

Trouton's rule states that the entropy of vaporization ($\frac{\Delta H_v^{\emptyset}}{T_b}$) is almost the same value, 85~88 J/(K·mol) [10], [12], for various kinds of liquids at their boiling points. Although it is based on the Gibbs potential $\Delta G = 0$, $\Delta H_v^{\emptyset}$ and T_b are measured independently. Hence, ΔS_v may be comparable to the

data in Tab. 1-4. Tab. 5 shows the results.

Table 5, Comparison of entropy calculated in this paper and from Gibbs potential

Gas	R×(A+3/2) J/(K·mol)	Latent Heat (kJ/mol)	T_b (K)	Trouton's ΔS_v J/(K·mol)
Ar	36.7	6.53	87.15	74.9
Kr	36.7	9.03	121.2	74.5
Xe	36.8	12.6	165.2	76.3
N_2	38.5	5.58	77.15	72.3
O_2	39.4	6.82	90.15	75.7
CO	39.8	6.0	81	74.1
F_2	41.8	6.32	85.15	74.2
H_2S	43	18.6	243	76.5
CO_2	48	16.7	288	58.0
SO_2	53.4	24.9	263	94.7
H_2O	56.8	40.68	373.15	125
NH_3	56.7	23.5	239.0	98.3
CF_4	34.3	12.1	212	57.1
CH_4	37	8.17	111.7	73.1
C_2H_6	46.5	14.7	194.1	75.7
n-C_3H_8	54.6	19.04	231.1	82.4
n-C_7H_{16}	64.3	31.77	371.6	85.5
n-C_8H_{18}	65.3	34.41	398.8	86.3
n-C_9H_{20}	69.4	36.91	424	87.1
CH_2=CH_2	44.5	13.54	169.4	80
Propene	54.1	18.42	225.5	81.2
Propyne	48.1	21.9	374	58.6
Benzene	48.7	30.77	353.25	87.1
Toluene	60.4	33.18	383.8	86.5
CH_3OH	70.3	37.49	337.7	111
C_2H_5OH	75.4	38.8	351.5	110
n-C_3H_7OH	73.8	41.44	370.3	112
i-C_3H_7OH	76.2	39.85	355.4	112

As shown in Tab. 5, Trouton's entropy is only found in some long-chain alkanes, benzene, and toluene. An interesting observation is that the entropy of small molecules calculated from Gibbs's potential is approximately twice that calculated in this paper. For example, this paper gives the entropy of 36.7 J/(K·mol) to Ar, whereas Trouton's entropy is 74.9 J/(K·mol).

This result reveals flaws in classical thermodynamics. The first law of thermodynamics states that the total energy of a thermodynamic system consists of its kinetic, potential, and internal energy. However, in classical thermodynamics, as the state changes, only the variation of internal energy is considered, equal to the variation of total energy, assuming that the variations of kinetic and potential energies are zero. This flaw results in the second law of thermodynamics, i.e., entropy increasing, to satisfy the requirement of energy conservation, because, as reported above, the variation in kinetic and

potential energy is nonzero. Since the surroundings must maintain the isolation of an isolated system, they require more energy than the system exhausted.

Gibbs's potential suggests the minimum ΔG at equilibrium, but it doesn't imply ΔG = 0. Assumedly realizing the heat equilibrium of a gas system, namely that the exothermic equals the endothermic, the exothermic quantity is $RTln\frac{V_G}{V_L}$. Under ordinary conditions, V_L can be considered a constant, and the variation in kinetic and potential energy is negligible. The equation of exothermic or endothermic quantity is similar to that of ΔG. That is why Gibbs potential has been widely applied.

Similarly, it may be inferred that Walden's entropy of fusion [8] should also have been overestimated.

Nevertheless, Walden's and Trouton's entropies are conceptually different from our entropy.

Another interesting observation is T_c*. Because P_c* is defined in our previous paper, [32] at the saturation,

$$\lim_{\substack{x_2\to 1\\ V_G^*\to 0}} \frac{1-x_2}{V_G^*} = \frac{10^{-3}P_C^*}{RT_C^*} \qquad (12)$$

It implies that, at extreme compression, the gas density is not infinite. Each gas has its own extreme density. Table 6 lists the extreme densities of some gases. It is obvious that alkanes have lower densities than the smaller gases. However, the physical significance of the extreme density is unclear.

Table 6. Extreme densities of some gases

Gas	T_c* (K)	P_c^* (MPa)	Ex. Density (mol/L)	Gas	T_c* (K)	P_c^* (MPa)	Ex. Density (mol/L)
He	8.72	0.434	5.988	CH_4	212.03	8.049	4.566
H_2	40.7	2.315	6.842	C_2H_6	324.5	7.803	2.892
D_2	44.85	2.926	7.846	n-C_3H_8	377.41	6.804	2.168
Ne	49.85	4.448	10.733	Cyclo-C_3H_6	435.83	6.163	1.701
Ar	167.21	8.252	5.936	n-C_4H_{10}	443.34	5.493	1.490
Kr	233.24	8.993	4.638	i-C_4H_{10}	421.2	5.061	1.445
Xe	322.04	9.733	3.635	n-C_5H_{12}	483.96	4.597	1.143
N_2	139.63	5.706	4.915	2-Me-C_4H_{11}	505.66	4.235	1.007
O_2	169.23	8.369	5.948	n-C_6H_{14}	526.91	3.902	0.891
CO	145.97	5.740	4.730	neo-C_5H_{12}	467.62	3.541	0.911
F_2	155.98	8.369	6.453	Cyclo-C_6H_{12}	594.58	3.066	0.620
H_2S	405.62	14.476	4.293	2-Me-C_5H_{13}	496.08	9.066	2.198
COS	405.31	10.397	3.085	n-C_7H_{16}	555.09	5.945	1.288
N_2O	335.08	11.664	4.187	n-C_8H_{18}	589.23	5.438	1.110
NF_3	250.72	7.603	3.647	n-C_9H_{20}	610.96	5.374	1.058
CF_4	245.81	6.325	3.095	n-$C_{10}H_{22}$	635.08	6.703	1.269
CO_2	330.06	12.237	4.459	n-$C_{12}H_{26}$	672.32	4.901	0.877
SF_6	343.46	5.933	2.078				
NH_3	435.57	18.982	5.242				
SO_2	458.05	12.942	3.398				
H_2O	696.45	40.711	7.031				

D_2O	691.54	40.467	7.038

Helium-4 Superfluid

In the above discussion, helium is not mentioned because its behavior is weird. It should be noted that the data on helium-4 in the technical note [35] has been adopted. By comparison with the data in the NIST Chemistry WebBook, it is found that WebBook digested the technical note data from 2.18 to 5.20 K.

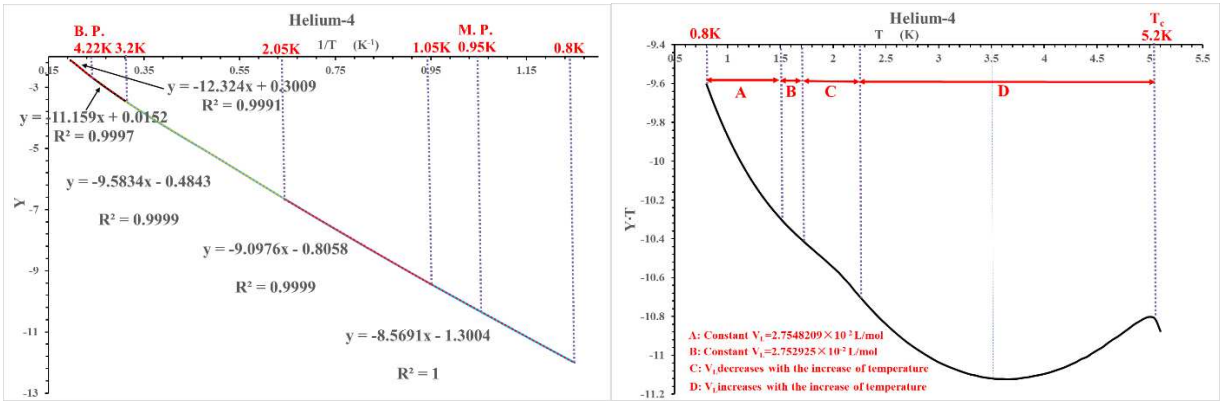


Figure 9, Y~$1/T$ and $Y{\cdot}T$~T curves of helium-4

As shown in Fig. 9, at first, it is disturbing in mathematics that the $Y{\cdot}T$~T curve is not a straight line, in contrast to the other gases so far concerned, in which both Y~$1/T$ and $Y{\cdot}T$~T curves are straight lines, and the linear regressions give similar results. Moreover, A is negative. For example, 4.22-5.20 K, A=0.3009; 3.2-4.22 K, A=0.0152; 2.05-3.2 K, A=-0.4843; 1.05-2.05 K, A=-0.8058; 0.8-1.05 K, A=-1.3004. This means that the entropy of a liquid or solid is greater than that of a gas at the same temperature.

Liquid helium is a superfluid with zero viscosity, which flows without losing kinetic energy. [36]-[38] When stirred, superfluid forms vortices that rotate indefinitely. The viscosity of superfluid helium can be understood in the classical two-fluid model, where only the normal fluid contributes to the viscous response. The abrupt drop in the mobility of electrons leads to a change in the solvation structure: the electron becomes localized and forms a sizeable spherical cavity ("bubble") in the medium. [36] However, it is hard to imagine that the positively charged nuclei are dissolved in the negatively charged electrons. From the viewpoint of orbital symmetry, the following atomic orbital shape change is depicted in this paper. As shown in Fig. 10, assuming that the shape of helium in gas is elliptic, whereas in the interval 4.2-5.2 K, it is spherical, we get n=2 for gas and n=1 for liquid. After that, the shape changes as the temperature decreases. In addition, helium's mobility in liquid increases as the temperature decreases. Hence, A values become negative.

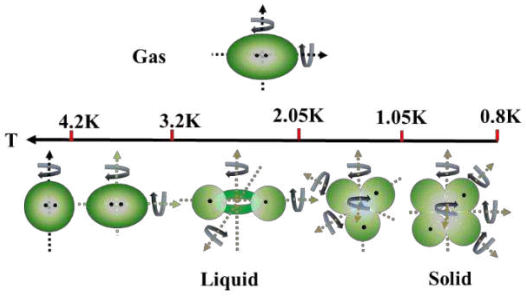


Figure 10, Shape changes of helium atomic orbital at low temperature

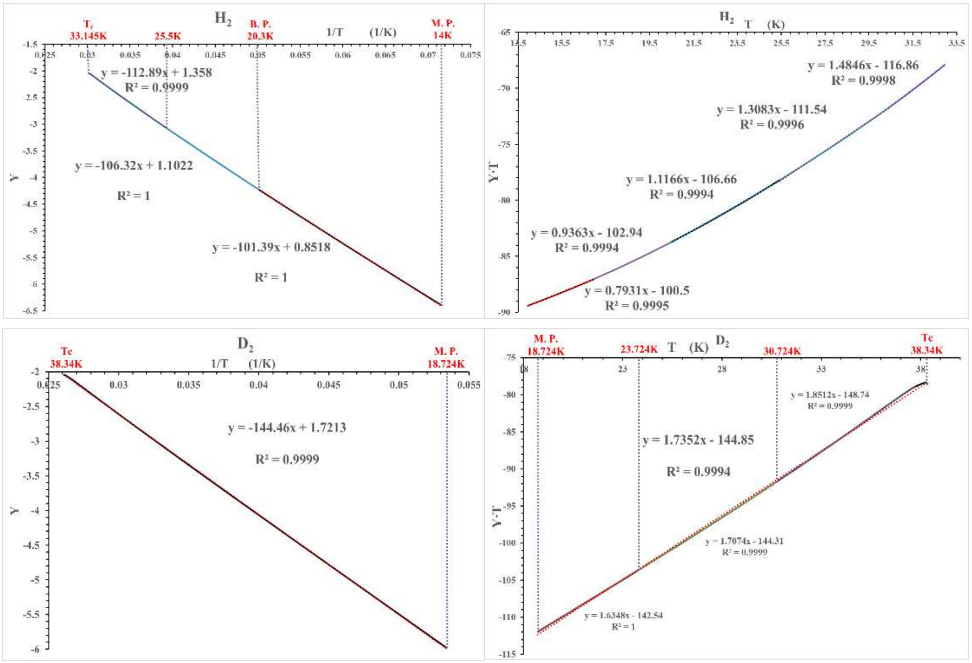


Figure 11, Y~1/T and $Y{\cdot}T$~T curves of H_2 and D_2

In H_2 and D_2, A decrease is also observed as the temperature decreases. As shown in Fig. 11, for H_2, A=1.48 in the region of T_c, but A=0.79 in the area of M.P. As for D_2, the decrement of A is decreased considerably to 0.2. It implies that the mass of nuclei may relieve the particularity. On the other hand, comparing the $Y{\cdot}T$~T curves of He-4 (Fig. 9) and H_2, it is observed that, upon extrapolation to 0 K, the H_2 curve may exhibit a shape similar to that of He. That is, increasing entropy near 0 K is expected for all gases.

It is rational that the mobility of electrons decreases near 0 K [37]. However, the assumption must be clarified that the positively charged nuclei dissolve in a solvent of the negatively charged electrons [38]. This assumption implies that the electron and the nucleus are electroneutral, consistent with the results reported in our previous paper [31].

Conclusion

In the paper, linear regressions of $\frac{\varepsilon_{exo}}{RT} \sim \frac{1}{T}$ on all the substances, for which NIST has issued the thermodynamic data, give a universal equation of heat, $\varepsilon_{exo} = B - \frac{3+2A}{2}RT$, where B represents the heat delivered by, theoretically, complete liquefaction of 1 mole gas. It equals the latent heat of evaporation, ΔH_v^{Φ}. After analyzing the relationship between the number of symmetry operations and the A values, it is observed that A reflects the symmetry of the quantized atomic/molecular orbital at the ground state: the smaller A and bigger D^2, the more symmetric the molecule. Using inert atoms as examples, the symmetry operation number of the 3 p^2 orbitals is 7; correspondingly, the A values of Ne, Ar, Kr, and Xe are 2.5518, 2.9104, 2.9140, and 2.9178, close to 7/2. Meanwhile, the tetrahedron of C sp^3 gives the operation number n=8; thus, for CH_4, A=2.9519. Based on this principle, in contrast

to the common sense of the geometric symmetry of atomic mass, CO is more symmetric than CO_2; H_2S and NH_3 are more symmetric than their counterparts, H_2O and NF_3. Moreover, the similarity in *A* between ethane and ethylene, propane and propylene, etc., suggests that the C-C π bond should be rotatable rather than rigid. Assuming each operation gives 1/2 *RT*, the remaining energy in liquid is (*n*/2-*A*) *RT*, provided that a free gas molecule owns all the operation numbers. Meanwhile, defining $\frac{3+2A}{2}R$ as the condensation entropy, it is observed that the entropy is about half of the entropy derived from Gibbs's free energy, i.e., $\Delta G = 0$. This result reveals flaws in classical thermodynamics that only consider the variation of internal energy, but neglect the variation in kinetic and potential energy. Indeed, the exothermic heat of liquefaction is not equal to the endothermic heat of evaporation. The Clausius-Clapeyron equation is derived from the equations of exothermic heat. Helium-4 superfluid exhibits an abnormal increase in entropy in the liquid as *T* decreases from 3.5 to 0.8 K. A similar trend in the linear regression curve of H_2 as the temperature approaches 14 K suggests that the entropy increase in liquid is a common phenomenon as the temperature approaches 0 K.

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The numerical data from Figures 2–12 (except for Fig. 1, Fig.7, and Fig. 11) and Tables 1-5 are calculated with Eq. 9 by citing the gas-liquid saturation data issued by NIST Chemistry WebBooK. Microsoft Excel is employed for the calculations and regressions.

References

[1]. Brown, R. J. C. R.; Brown, F. C. Melting Point and Molecular Symmetry. *J. Chem. Ed.* **2000**, *77 (6)*, 724-731.

[2]. Pinal, R. Effect of molecular symmetry on melting temperature and solubility. *Org. Biomol. Chem.* **2004**, *2*, 2692 – 269.

[3]. Wyttenbach, N.; Niederquell, A.; Kuentz, M. Machine estimation of drug melting properties and influence on solubility prediction. *Mol. Pharm.*, **2020**, *17(7)*, 2660-71.

[4]. Lopez, D. H.; Yalkowsky, S. H. The Relationship Between Molecular Symmetry and Physicochemical Properties Involving Boiling and Melting of Organic Compounds. *Pharm. Res.*, **2023**, *40*:2801-2815.

[5]. Dearden, J.C. Quantitative structure-property relationships for prediction of boiling point, vapor pressure, and melting point. *Environ. Toxic. Chem.* **2003**, *22(8)*:1696-709.

[6]. Ezra, G. S. On the symmetry properties of non-rigid molecules: A unified approach. *Mol. Phys.*, **1979**, *38(3)*, 863-875.

[7]. Yalkowsky, S. H.; Krzyzaniak, J. F.; Myrdal, P. B. Relationships between Melting Point and Boiling Point of Organic Compounds. *Ind. Eng. Chem. Res.* **1994**, *33*, 1872-1877.

[8]. Walden, P. Über organische Lösungs-und Ionisierungsmittel. III. Teil: Innere Reibung und deren Zusammenhang mit dem Leitvermögen. *Z. Phys. Chem.,* **1906**, 55, 207-246.

[9]. Yalkowsky, S.H. Estimation of entropies of fusion of organic compounds. *Ind. Eng. Chem. Fundam.* **1979**, *18*, 108-111.
[10]. Trouton, F. On Molecular Latent Heat. *Philosophical Magazine*, **1884**, *18 (110)*, 54-57.
[11]. Hildebrand, J.H. The Entropy of Vaporization as a Means of Distinguishing Normal Liquids. *J. Am. Chem. Soc.*, **1915**, *37(5)*, 970-978.
[12]. Myrdal, P. B.; Krzyzaniak, J.F.; Yalkowsky, S. H. Modified Trouton's rule for predicting the entropy of boiling. *Ind. Eng. Chem. Res.*, **1996**, 35(5), 1788-92.
[13]. Joback, K.G.; Reid, R.C. Estimation of pure-component properties from group-contributions. *Chem. Eng. Commun.*, **1987**, *57(1–6)*, 233-243.
[14]. Ma, P., Zhao, X. Modified group contribution method for predicting the entropy of vaporization at the normal boiling point. *Ind. Eng. Chem. Res.,* **1993**, *32(12)*, 3180-3183.
[15]. Stein, S.E.; Brown, R.L.; Estimation of normal boiling points from group contributions. *J. Chem. Inf. Comput. Sci.*, **1994**, *34(3)*, 581-587.
[16]. Constantinou, L.; Gani, R. New group contribution method for estimating properties of pure compounds. *AIChE J.*, **1994**, *40(10)*, 1697-710.
[17]. Cao, D.; Feng, X.; Wang, Q.; Jia, Q.; Xia, S.; Yan, F. Atomic Connectivity Group Contribution Method for Predicting the Phase Transition Properties of Enthalpy and Entropy. *Ind. Eng. Chem. Res.* **2023**, *62*, 13701−13709.
[18]. Dannenfelser, R. M.; Surendran, N.; Yalkowsky, S. H.; Molecular Symmetry and Related Properties. *SAR* and *QSAR in Envir. Res.*, **1993**, *I*, 273-292.
[19]. Gilbert, A. S. Entropy-enthalpy compensation in the fusion of organic molecules: implications for Walden's rule and molecular freedom in the liquid state. *Thermochimica Acta*, **1999**, *339* 131-142.
[20]. Jones, M. In *Organic Chemistry*, W. W. Norton: New York, **1997**.
[21]. Wei, J. Molecular Symmetry, Rotational Entropy, and Elevated Melting Points. *Ind. Eng. Chem. Res.* **1999**, *38*, 5019-5027.
[22]. Waiters, A. E.; Myrdal, P. B.; Yalkowsky, S. H. A Method for Estimating the Boling Points of Organic Compounds from Their Melting Points. *Chemosphere*, **1995**, *31 (4)*, 3001-3008.
[23]. Clausius, R.J.E. On a Mechanical Theorem Applicable to Heat. *Philosophical Magazine*, **1870**, *4th Series. 40*: 122–127.
[24]. Dunitz, J. D. Symmetry arguments in chemistry. *Proc. Natl. Acad. Sci. USA*, **1996**, *93*, 14260-14266.
[25]. Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry,* Verlag Chemie, Weinheim, Germany, **1970**.
[26]. Estrada, E.; Avnir, D. Continuous Symmetry Numbers and Entropy. *J. Am. Chem. Soc.* **2003**, *125*, 4368-4375.
[27]. Lord Jr., R. C.; Andrews, D. H. Entropy and the Symmetry of the Benzene Molecule. *J. Phys. Chem.* **1937**, *41*, 1, 149–158.
[28]. Ni, H.-M.; Zhu, B. A new general state equation of real gases. *ChemRxiv*, **2022**, DOI: 10.26434/chemrxiv-2022-5m718-v4. Accessed date: Feb. 27, 2026.
[29]. Ni, H.-M. On the Hydrophobic Hydration, Solvation and Interface: A Thought Essay (I). *J. Mol. Liquids*, **2022**, *368*, 120690.
[30]. Cui, X.-Y.; Zhu, B.; Ni, H.-M. A New Model for Specific Heat Capacity of Real Gas. *ChemistrySelect*, **2024**, 9, e202304699 (1 of 10).

[31]. Ni, H.-M. Unified Mechanics on Thermodynamics, Classical Mechanics, and Quantum Mechanics. *ChemRxiv*, **2024**, DOI: 10.26434/chemrxiv-2024-35kds-v7. Accessed date: Feb. 27, 2026.
[32]. Cui, X.-Y.; Liu, L.Y.; Shao, Q.F.; Ni, H.-M. Simplified State Equations at Saturation and Isotherm. *ACS Omega*, **2025**, DOI: 10.1021/acsomega.4c10390.
[33]. The Engineering Tool Box, https://www.engineeringtoolbox.com/ice-thermal-properties-d_576.html. Accessed date: Feb. 27, 2025.
[34]. Zhang, Y.; Evans, J.R.G.; Yang, S. Corrected Values for Boiling Points and Enthalpies of Vaporization of Elements in Handbooks. *J. Chem. Eng. Data*, **2011**, *56*, 328-337.
[35]. Arp, V. D.; McCarty, R. D.; Friend, D. G. Thermophysical Properties of Helium-4 from 0.8 to 1500 K with Pressures to 2000 MPa. *NIST Technical Note 1334* (revised), U.S. Government Printing Office, Washington DC: **1998**.
[36]. Darrow K.K., *Rev. Mod. Phys.* **1940**, *12*, 257-266. Helium is the superfluid.
[37]. Townsend A.A., J. *Fluid Mechanics*, **1963**, *15(2)*, 262-272. On the hydrodynamic equations for flow of liquid helium II with mutual friction.
[38]. Aitken F., Volino F., Mendoza-Luna L. G., von Haeften K., Elorant J., *Phys. Chem. Chem. Phys.*, **2017**, *19*, 15821. A thermodynamic model to predict electron mobility in superfluid helium.

ToC

