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Refining the Diatomic Model for the Vaporization of Liquids

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Abstract: Pair-wise interaction models are frequently used to describe the behavior of complex processes to facilitate conceptualization, even if the numerical predictions may only be approximate. Such a model describing the forces of vaporization in liquids has been suggested by Prebeg. When applying such heuristic models it is important delineate their range of applicability. Prebeg's model has been modified and applied to the vaporization of a number of hydrocarbons. The modified model provides quantitative agreement with experimental results for the vaporization of these hydrocarbons.

Keywords: condensation forces, vaporization, hydrocarbons

Introduction

Prebeg [1], [2] has proposed a simple model describing the cohesive forces in liquids. He modeled vaporization⁽¹⁾ as a process in which:

- The cohesive forces governing the structure of the liquid phase can be approximated by a two-body (diatomic) interaction.
- The vapor is an ideal gas, with the molecules free to move in three directions with a translational kinetic energy, $E_{3D} = 3/2 kT$ – a consequence of the kinetic theory of gases.
- Molecules in the liquid phase move freely in two directions with kinetic energy, $E_{2D} = kT$, but are constrained in the third direction by a cohesive force, F .
- Molecules in the solid phase are constrained by an average isotropic cohesive force and are not free to translate in any direction.

Applied to the liquid \rightarrow vapor transition, his model leads to an energy change:

$$\Delta E_{L \rightarrow V} = 3F(X_V - X_L) + \frac{1}{2} k T_{L \rightarrow V} \quad (1)$$

Where: $\Delta E_{L \rightarrow V}$ is the heat of vaporization at the “normal” boiling point ($P = 1 \text{ atm.}$), F is an average one dimensional intermolecular force, X_V and X_L are an average intermolecular distance between species in the vapor and liquid respectively. The term $\frac{1}{2} k T_{L \rightarrow V}$ accounts for the increase in one degree of translational freedom upon vaporization. Since $X_V \gg X_L$,

equation (1) was further simplified and resulted in expressions for X_V and F in terms of experimentally measurable quantities. At the normal boiling point:

$$X_V = (6 \times V_{BP} / \pi)^{1/3} \quad (2)$$

and:

$$F = (\Delta E_{L \rightarrow V} - \frac{1}{2} k T_{L \rightarrow G}) / 3 X_V \quad (3)$$

Prebeg applied the model to the vaporization of the elements in the periodic table for which data are available. He concluded that the condensation force, F , is independent of the nature of the particular element, and that substances could be considered as being organized in diatomic pairs held together by a “universal” condensation force that is proportional to the volume of interaction, ($\sim X_V^3$). One might contend that since the model invokes a force in the liquid in only one direction that the coefficient “3” in equation (3) should be “1”, but this is only a matter of scaling, and doesn’t affect the gist of the model. The factor “3” is retained here to remain consistent with his analysis.

It is important not to overextend the range of application of a model such as this. Such a simple model for the liquid state, while useful, must be very approximate because the liquid state is very complex and each of the assumptions of the model fails under certain conditions. For example:

1. Prebeg’s conclusion that the condensation force is “universal” (i.e. independent of the nature of the substance and proportional to the volume of interaction) is based upon a plot of “ F ” vs. “ X_V^3 ” for many elements of the periodic table. However, because of the scatter in the data it is not clear that a cubic dependence is optimal. Possibly the data could be fitted as well by a quadratic, a quartic, or even some fractional exponent of X_V .
2. Chemically, it is unrealistic to expect that the force governing the vaporization of a refractory metal such as tungsten and a rare gas such as helium is the same. In addition, no *molecules* were used to test the model. It is clear that the forces governing the vaporization of molten ionic salts and of covalently bonded organic liquids are very different.
3. Caution must be exercised when drawing conclusions from graphs of data. For example, combining all the elements together in a single graph as Prebeg does [1] may obscure correlations present for chemically related substances. That is, the data in his figure (4) could be a series of unresolved overlapping straight lines for chemically related elements. An example of an analogous effect is the graph of a polygon with a large number of sides. On a sufficiently small scale, the graph of the polygon may appear circular even though the perimeter of the figure is actually comprised of straight lines.
4. The assumption that no motion occurs in the solid state fails for the numerous substances that have solid state transitions. Some substances (e.g. phosgene) exhibit multiple melting points even at ambient pressure. [3]
5. The assumption that the liquid state corresponds to free motion in two directions precludes viscosity as a property of liquids, since viscosity depends precisely on forces operating against the directions of motion of a liquid. Surface tension also depends upon similar forces.
6. To assume that the vapor is ideal implies non-interacting point masses. However, the phenomenon of vaporization against a cohesive force demands some sort of interaction

between the particles, even in the vapor phase. For most vapors at moderate pressures, say less than a few atmospheres, this force is attractive, so $V_{BP} < V_{IDEAL}$.

7. The source of repulsion is described in reference [2] as “electro-magnetic force”; however, the term is not defined in more detail. This is ambiguous because there are many “kinds” of “electromagnetic force”. There are various *attractive* forces proportional to various powers in a series expansion of the potential energy $U(R) \sim -1/R^n$, where R is the interatomic separation, and $n = 1$ to 6, depending upon the specific electronic interaction involved. The “repulsive” part of the potential energy is a very complicated function of the detailed collective quantum mechanical behavior of the electrons. Depending upon the particular analysis, this is approximated by a potential energy $U(R) \sim +1/R^N$, where $N \cong 12$, or $U(R) \cong + \exp(-\alpha \times R)$. The particular functional form is selected more to facilitate computation than to represent the detailed electronic interactions. The only requirement is that $U(R)$ increase rapidly with decreasing “ R ”. These interactions are not Coulombic repulsion, but are related to the Pauli Exclusion Principle. These matters are discussed in detail in a number of texts, for example reference [4].

Modifications

It is clear that this simple model is approximate, and applying it to all of the elements in the periodic table is perhaps too broad. The cohesive forces of various liquid substances differ widely. For example, water and neon are isoelectronic, both have 10 electrons, but because of their very different molecular structure, the boiling point of water is 373 K, while the boiling point of neon is only 27 K. Applying a modification of Prebeg’s reasoning to a narrower class of *similar* substances provides a clearer test of the model. The following modifications to the model are made:

1. Hydrocarbons are considered. These are a smaller class of compounds where the forces governing vaporization are similar and reliable data are available for a large variety of molecular weights, shapes, and structures.

2. The analysis parallels Prebeg’s; however, the results are recast in terms of the intermolecular potential energy, $U(X)$, rather than in terms of the intermolecular force, $F(X)$, used by Prebeg. The two quantities are related by the definition: $F(X) = -\partial U(X)/\partial X$, but the formalism in terms of potential energy is more customary. As a consequence:

$$U(X) = - \int F(X) d(X) \quad (4)$$

If $F(X)$ is linear as Prebeg proposes, that is $F(X) = A \times X$, then $U(X)$ will be quadratic in the variable X :

$$-U(X) = \frac{1}{2} A \times X^2 + B \times X + C \quad (5)$$

3. The ideal gas law is abandoned because the same intermolecular forces responsible for the formation of the liquid phase are responsible for non-ideality in the vapor phase, so it is appropriate to incorporate non-ideality of the vapor into the model. There are numerous equations of state of real gases to choose from. Here, an equation of state proposed by Berthelot is used to calculate the volume of the vapor V_{BP} at the normal boiling point needed in equation (2):

$$PV = RT + 9RPT_c/128P_c (1 - 6(T_c/T)^2) \quad (6)$$

This choice is made for algebraic simplicity, because experimental values of the critical constants, T_c and P_c are available, and no other fitting parameters are required. Also, Berthelot's equation has been used by many careful experimentalists where modest corrections for the non-ideal behavior of gases are needed in thermodynamic calculations. [5], [6].

4. The molecular shapes of hydrocarbons affect their volatility. Generally, hydrocarbons are not spherical, so somehow this effect needs to be taken into account. Pitzer et. al. [5] has developed a theory of "normal fluids" which introduces an empirical correction for non-sphericity called the acentric factor, ω . It is defined in terms of the critical temperature, T_c , and critical pressure, P_c :

$$\omega = -\log(P_s/P_c) - 1.000 \quad (7)$$

where P_s is equal to the vapor pressure of the substance at a reduced temperature, $T_r = T/T_c = 0.700$. Pitzer selected this value so that $\omega = 0$ for the spherical inert gases Ar, Kr, and Xe. For methane, CH_4 , $\omega = 0.7032$, which means methane is essentially spherical. The value 0.7032 was used in the calculations here.

Analysis and Discussion

The data used in the calculations were obtained from the National Institute of Science and Technology (NIST) website [7]. In all 22 hydrocarbons were used – 6 unbranched "normal" alkanes (methane through hexane), 13 branched alkanes, and 3 alkenes. Hydrocarbons with linear chain lengths greater than 6 were excluded because chain entanglement becomes increasingly important in the liquid phase when the length of a linear part of a hydrocarbon chain exceeds 6 carbon atoms, and chain entanglement is not taken into account in this model.

The vapor pressure used in equation (7) was computed from Antoine's equation:

$$\log_{10}(P_{\text{atm}}) = A - (B/(T+C)). \quad (8)$$

T is in kelvins, and the constants A , B , and C are from reference [7]. The vapor volume at the boiling point was calculated from equation (6). These factors were combined to calculate an acentric intermolecular distance, $X_V\omega$.

The energy of vaporization, $U(X_V\omega)$, was then calculated from equation (5). The corresponding expression for the condensation force used by Prebeg is:

$$F(X_V\omega) = \{(\Delta H_{L \rightarrow V} - \frac{1}{2} k T_{L \rightarrow G}) / 3 X_V\omega\} \quad (9)$$

Note that the more generally accepted notation for enthalpy of vaporization, $\Delta H_{L \rightarrow V}$, (the heat of vaporization of the liquid at 1 atm. pressure) replaces the term $\Delta E_{L \rightarrow V}$ used by Prebeg.

Conclusions

Figure 1 is a plot of $U(X_V\omega)$ as a function of $(X_V\omega)$. The least squares fit of the data is quadratic:

$$U(X_V\omega) = -0.0348 + 0.8508 \times (X_V\omega) + 0.3046 \times (X_V\omega)^2 \quad (10)$$

The correlation coefficient, $R = 0.98$. A scatter plot of the residuals (Figure 2) indicates the errors are randomly distributed.

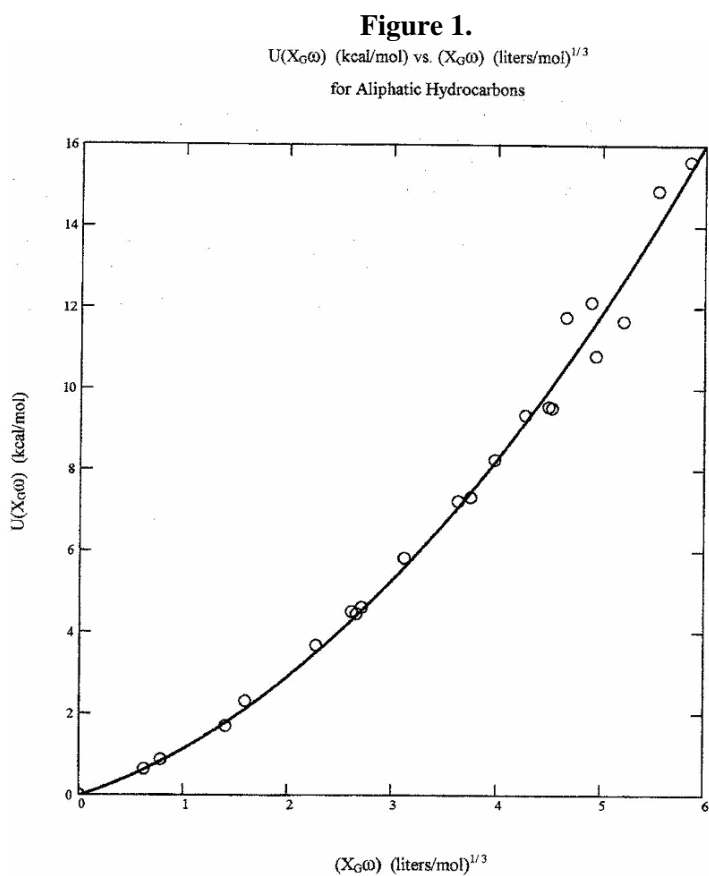
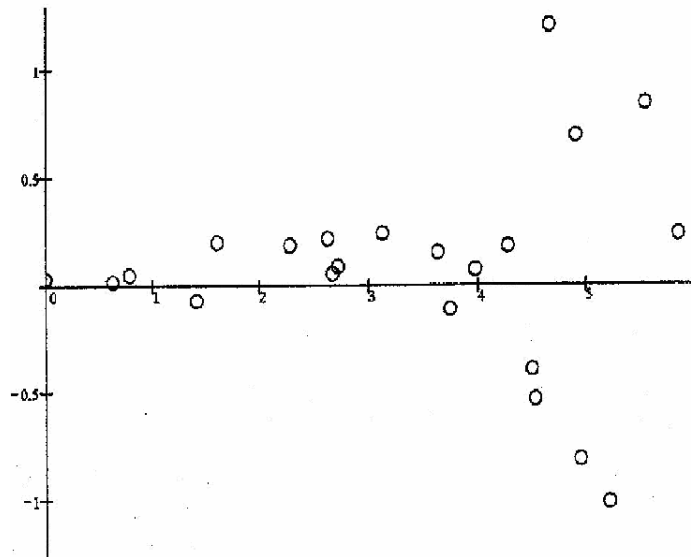


Figure 2.

Scatter Plot of (observed - calculated) Values of
 $U(X_G\omega)$ (kcal/mol) vs. $(X_G\omega)$ (liters/mol)^{1/3}



The intercept $U(0) \cong 0$ as it should be for spherically symmetric CH_4 . It is clear that the “cohesive force” is *proportional to* the intermolecular distance ($X_V\omega$) rather than the cubic dependence suggested by Prebeg. A linear relation of the “cohesive force” and distance is what one expects from simple considerations. Specifically, the “cohesive force” (i.e. restoring force) for *any* diatomic model should be a harmonic oscillator as a first approximation.

The simple diatomic model proposed by Prebeg appears to be reasonable for modeling the vaporization of liquids in terms of experimental parameters that are usually known. However, the “cohesive force” is not a universal force. More likely it applies to families of chemically similar substances.

Footnotes:

- (1) Prebeg uses the term “condensation force”. The related term “vaporization energy”, defined in the text, is more commonly used.
- (2) The units of $(X_G\omega)$ and $U(X_G\omega)$ in Table I have been left in their “natural” units “closest” to the source data, (liters)^{1/3} and (kcal/mol) respectively. The value: $(X_G\omega) = 2.820$ for an ideal gas at standard conditions ($T = 273.15$ and $P = 1$ atm) is a useful reference point for abscissa $(X_G\omega)$. The values in the table multiplied by 5.5×10^{-7} and 6.9×10^{-14} respectively converts the values to (cm) and (ergs/molecule) respectively.

Table I.
Data for Hydrocarbons ⁽²⁾

Hydrocarbon	$X_{G\omega}$ (liters/mol) ^{1/3}	$U(X_{G\omega})$ (kcal/mol)	(calc.)	(obs.- calc.)
methane	0.000	0.000	-0.035	0.035
ethene	0.627	0.639	0.619	0.020
ethane	0.786	0.873	0.822	0.051
propene	1.405	1.690	1.761	-0.071
propane	1.593	2.295	2.093	0.201
propane, 2-methyl-	2.275	3.662	3.476	0.186
propane, 2,2-dimethyl-	2.618	4.498	4.280	0.218
1-butene	2.663	4.447	4.391	0.056
n-butane	2.715	4.608	4.519	0.089
butane, 2-methyl-	3.118	5.823	5.580	0.243
butane, 2,2-dimethyl-	3.629	7.218	7.064	0.154
n-pentane	3.745	7.310	7.422	-0.112
butane, 2,3-dimethyl-	3.975	8.235	8.160	0.075
butane, 2,2,3-trimethyl-	4.271	9.336	9.154	0.182
pentane, 3-methyl-	4.495	9.549	9.944	-0.396
pentane, 2-methyl-	4.527	9.523	10.060	-0.538
pentane, 3,3-dimethyl-	4.661	11.755	10.548	1.207
pentane, 2,2-dimethyl-	4.899	12.136	11.442	0.693
n-hexane	4.944	10.804	11.618	-0.814
pentane, 2,4-dimethyl-	5.212	11.661	12.674	-1.014
pentane, 2,2,4-trimethyl-	5.540	14.870	14.026	0.845
hexane, 2-methyl-	5.849	15.595	15.361	0.234

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