

A New Constant from Classical Nucleation Theory

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ABSTRACT:- Blander and Katz give a formula in classical nucleation theory, $J = A \exp K$, for homogeneous nucleation (liquid-->gas). Jennings proved that $d \ln A / dK = 1/6K$ for all pure liquids by combining two theories, taking the limit as polymer concentration-->0. This gives $\ln A = (1/12) \ln(K^2) + C$, where C is the integration constant. The conjecture is that C is a constant for fluids of low molecular weight. We used data for 10 sample solvents, and solved for C. The surface tension drops out in C, which makes C more accurate, as the surface tension is difficult to get at $0.89T_c$, the limit of superheat. T_c = critical point in Kelvin. All quantities are evaluated at the limit of superheat, which is approximately $0.89T_c$ for solvents. $C = 75.379 \pm 1.073$ for the 10 solvents (a range of polar to non-polar). This eliminates the prefactor A, streamlining J: $\ln J = (1/12) \ln(K^2) + 75.379 + K$ is the exact new equation. Using information from Blander and Katz, it is possible to get an exact value for K. $K = -64.5605$.

KEY WORDS:- “homogeneous nucleation” “Flory-Huggins theory” “limit of superheat” “differential equation” “polymer solutions”

I. INTRODUCTION

In the late 1800s, Josiah Willard Gibbs had the idea that there's a trade-off between lowering energy and maximizing entropy where clusters of a new phase appear driven by the increase in temperature to overcome the barrier to forming a new phase. In 1942, Flory and Huggins made a theory for the mixing of polymer and solvent based on a lattice model. This paper shows how they join in a new way.

Over the years since Gibbs, homogeneous nucleation has been studied and developed into an exact theory that gives a well-defined nucleation rate with a prefactor multiplied by an exponential term. The prefactor slowly varies with rising temperature and in this paper, the author presents an exact derivation supported by data that allows for elimination of the prefactor.

THEORY

Later on, these two trains of thought developed into 1) modern classical nucleation theory (CNT) as put forth by Blander and Katz 1975 and 2) the model for surface tension of polymer solutions (STPS) refined by Siow and

Patterson 1973. In 2012, Jennings combined the CNT/STPS equations and that later led to equation (19) in Jennings 2014, here as (1), a general formula for bubble nucleation in polymer solutions. The data for (1) was first presented in graphical form in Jennings and Middleman 1985.

$$\Delta T = 3kT^2_w MW_1 / \sigma a MW_2 \quad (1)$$

Blander and Katz's (15) is the abbreviated formula (2) here for the nucleation rate,

J, discussed in Appendix 1.

$$J = A \exp K \quad \text{bubbles/cc-sec} \quad (2)$$

Jennings 2012, proved in (11) there, essentially that

$$d \ln A / dK = 1/6K \quad (3)$$

for all pure liquids by combining the CNT/SPTS theories and then taking the limit as polymer concentration $\rightarrow 0$. See Appendix 2 for an outline of the 2012 proof for Eq.

(3), which is the precursor to Eq. (1). The solution to Eq. (3) is

$$\ln A = (1/12)\ln(K^2) + C \quad (4)$$

where C is the integration constant. Notice K is squared because K is a negative number. C is a pure number, the same for 10 fluids, as equation (3) is general.

II. METHODOLOGY

In the early 1980s, Jennings and Middleman collected data on liquid \rightarrow gas nucleation as affected by presence of polymer. In 2012, Jennings made a foray into a theoretical treatment that predicts the early 1980s data quite well. In Jennings' 2012 paper is contained the starting equation for this work, more clearly laid out in

Appendix 2. This is Eq. (3), a truly exact formula, which has a well-defined integration constant, putting the whole theory on solid ground.

The pre-exponential factor, PEF, has been studied and was derived years ago. There is a paper by Shiao 2018, where the temperature dependence of the PEF was investigated. Eq. (3) is the precursor to Eq. (1). Bovey and Winslow 1979 give an exact equation for boiling point elevation due to addition of polymer, where the heat of vaporization appears in denominator instead of the surface tension, but otherwise that equation is similar to Eq. (18) in Jennings 2012.

A preliminary study to this effort was published by Jennings 2019 with seven solvents and this paper has more solvents and brings classical nucleation theory to its logical conclusion and includes the clearer derivation of the starting Eq. (3) in

APPENDIX 2. The author feels that the additional solvents and results justify a new paper and this is of interest in the field of thermodynamics and chemical engineering.

III. RESULTS AND DISCUSSION

The reason for undertaking this work was when we noticed that the integration constant varied little among different solvents. This is interesting because: 1) equation (3) is mathematically correct and exact for pure liquids and 2) the integration constant C should be a universal constant as long as BLANDER/KATZ's equation (2) holds. This is true as long as the Poynting correction is valid, that is, the vapor pressure of the solvent is appreciably greater than the ambient pressure. Remember, equation (2) is evaluated only at the limit of superheat for all quantities because Blander/Katz's formula is to give the limit of superheat for liquids. The novelty of this study is that a strange formula, equation (4), gives a novel new constant in physical chemistry, based on (15) in BLANDER/KATZ's highly cited paper.

C was then evaluated with data at the limit of superheat for ten common solvents, inserting the data in (4) and solving for C. The surface tension cancels out in (4) and this is fortunate, as the surface tension is hard to estimate at 0.89 of the critical temperature, where the limit of superheat is.

Data

Here is a table of the calculations for C from July 27, 2019 until January 8, 2020.

Solvent (low MW)	C (integration constant)	δ (SI) solubility Hildebrand	MW gm/mol molecular weight
heptane	74.10	15.3	100.21
hexane	74.60	14.9	86.18
carbon tetrachloride	74.79	18.0	153.82
cyclohexane	74.82	16.8	84.16
pentane	74.84	14.4	72.15
cyclopentane	75.11	16.2	70.14
benzene	75.14	18.7	78.12

ethanol	75.91	26.2	46.07
methanol	76.54	29.7	32.04
water	77.94	48.0	18.02

The higher the solubility parameter is, there is a trend to higher C. The lower the MW is, there is a trend to higher C.

$$C = 75.379 \pm 1.073$$

Anyway, the results above show that C = constant through the range of sample solvents going from non-polar pentane to polar water. Notice there is little scatter. Some of the solvents are alkanes along with a variety up to polar solvents. It appears that C is a constant for low MW solvents. For Blander and Katz's formula in APPENDIX 1 and APPENDIX 2, this enables the prefactor A to be eliminated.

ln J becomes simply:

$$\ln J = (1/12)\ln(K^2) + C + K \quad (5)$$

See Appendix 1 for Blander and Katz's exact expression for J and details on the workup of the data. See Appendix 2 for derivation of Eq. (3), the starting equation.

For Eq. (5), the nucleation rate J is solely a function of K. Using a CASIO fx-115ES scientific calculator iterating with C = 75.379 and Blander and Katz's value (for nucleation of $J = 10^4 - 10^6$) the author took the geometric mean for J, and obtained equation (6). Getting the value for T (Kelvin) yields the temperature of liquid--> gas nucleation, which obviously needs a sophisticated computer program.

$$1830.84 = T (P_e - P_L)^2 \delta^2 / \sigma^3 \quad (6)$$

Finally, Blander and Katz say when the value of J changes by a factor of 1,000 to 10,000 the prediction of the limit of superheat changes only one degree Celsius.

So, the uncertainty in C is ± 1 , or only one power in the natural logarithm of J, a factor of e, a minuscule uncertainty. $K = -64.5605$ for the ten solvents.

IV. CONCLUSIONS

These results bear out that C is a strange new universal constant, which should be true for solvents of low molecular weight. Again, it needs to be borne in mind that the surface tension is hard to determine up at the limit of superheat and the surface tension conveniently drops out! This study is not concerned with direct calculation of the nucleation rate, but it is shown here that the pre factor in classical nucleation theory for liquid-->gas has been eliminated and K has been evaluated exactly for all solvents.

NOMENCLATURE

- a surface area of solvent molecule
- A prefactor
- B coefficient
- C constant of integration
- d density of liquid
- J nucleation rate
- k Boltzmann constant
- K exponent
- M molecular weight of liquid
- MW_i molecular weight: solvent 1, polymer 2
- P_e equilibrium vapor pressure
- P_L ambient pressure
- P_v vapor pressure

- T temperature Kelvin
- T_c critical temperature in Kelvin

w weight fraction polymer
 δ Poynting correction factor
 ΔT rise in superheat in Centigrade
 σ surface tension

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APPENDIX 1

1) $J = A \exp K$

$$J \approx 3.73 \times 10^{35} (d^2 \sigma / M^3 B)^{1/2} \exp [- 1.182 \times 10^5 \sigma^3 / (T (P_V - P_L)^2)]$$

A is the prefactor and K is the exponent, according to this detailed equation (15) in Blander/Katz.

2) There is a Poynting correction, δ , where

$$\delta \approx (P_V - P_L) / (P_e - P_L)$$

B is close to 2/3. δ and B are discussed in Blander/Katz.

3) In the detailed expression for J (bubbles/cc-sec) above, the other units are as follows: P_e (equilibrium vapor pressure), P_V (vapor pressure) and P_L (ambient pressure) are all in atmospheres; T is the limit of superheat for the solvent (Kelvin); σ is the surface tension (dynes/cm); in the pre factor, M is the molecular weight of solvent (g/mole); and d is its density (g/cc). All quantities are at the limit of superheat for each solvent.

4) Sources for the data were CRC Handbook, JASPER, ANTOINE EQUATION (Iran Website),

BLANDER/KATZ and various Internet websites for densities. However, the density of cyclopentane was estimated and also the limit of superheat of carbon tetrachloride was estimated. Admittedly, this is a bit imprecise, but the mathematics dictates that C is a pure number.

APPENDIX 2

Proof of $d \ln A / dK = 1 / (6K)$ for all pure liquids $J = A \exp K$ from Blander and Katz classical nucleation theory liquid \rightarrow gas.

The starting equations are from

1) Blander and Katz (Z) and 2) Siow and Patterson (A) and (B).

See JH Jennings, International Journal of Thermodynamics article, Ref. (10). page 127-128.

$$J \approx 3.73 \times 10^{35} (d^2 \sigma / M^3 B)^{1/2} \exp [- 1.182 \times 10^5 \sigma^3 / (T (P_V - P_L)^2)] \quad (Z)$$

$$(\sigma - \sigma_1) a / kT = \ln (\varphi_{1S} / \varphi_1) + ((r - 1) / r) (\varphi_{2S} - \varphi_2) \quad (A)$$

$$\ln [(\varphi_{2S} / \varphi_2)^{1/r} / (\varphi_{1S} / \varphi_1)] = (\sigma_1 - \sigma_2) a / kT \quad (B)$$

Now, near $\varphi_2 = 0$, Eq. (B) becomes

$$\varphi_{2S} = \varphi_2 \exp [r (\sigma_1 - \sigma_2) a / kT]$$

Putting in the numbers, $\partial \varphi_{2S} / \partial \varphi_2 \approx 10^{-38}$ for $MW_2 = 2000$, $r = 13.4$ and

even less for higher MW.

First, it is necessary to prove Eq. (11) in Ref. (10).

$$\lim_{w_2 \rightarrow 0} (\partial \ln A / \partial w_2) / (\partial K / \partial w_2) = 1 / (6K)$$

$$A = 3.73 \times 10^{35} \left(\frac{d^2 \sigma}{M^3 B} \right)^{1/2}$$

Omitting a few steps, because they are obvious and constants, we have

$$\partial \ln A / \partial w_2 = (1/d) (\partial d / \partial w_2) + (1/2\sigma) (\partial \sigma / \partial w_2) - (1/2B) (\partial B / \partial w_2)$$

In calculating $\partial K / \partial w_2$, we note that $\partial T / \partial w_2 = 0$, as T and w_2 are orthogonal.

P_L is ambient pressure and therefore is constant; δ is the Poynting correction factor.

$$K = -1.182 \times 10^5 \frac{\sigma^3}{(T(P_v - P_L))^2} = -1.182 \times 10^5 \frac{\sigma^3}{(T(P_e - P_L))^2 \delta^2}$$

$$\partial K / \partial w_2 = -1.182 \times 10^5 \frac{(3)\sigma^2 (\partial \sigma / \partial w_2)}{(T(P_e - P_L))^2 \delta^2} +$$

$$1.182 \times 10^5 \frac{(2)\sigma^3 (\partial P_e / \partial w_2)}{(T(P_e - P_L))^3 \delta^2} +$$

$$1.182 \times 10^5 \frac{(2)\sigma^3 (\partial \delta / \partial w_2)}{(T(P_e - P_L))^2 \delta^3}$$

We prove these four differentials are zero, which simplifies it, page 128 of Ref. (10).

$\partial \delta / \partial \phi_2 = 0$, $\partial d / \partial \phi_2 = 0$, $\partial P_e / \partial \phi_2 = 0$, and $\partial B / \partial \phi_2 = 0$ for w_2 near 0.

1. $d = d_1 + (d_2 - d_1) \phi_{2S}$

$$\partial d / \partial \phi_2 = (d_2 - d_1) (\partial \phi_{2S} / \partial \phi_2), \text{ which vanishes for } w_2 \text{ near } 0.$$

2. $P_e = P_e(0) \phi_{1S} = P_e(0) (1 - \phi_{2S})$

One can see by inspection that here $\partial P_e / \partial \phi_2$ also vanishes.

3. $B \approx 1 - 1/3 (1 - P_L/P_v)$ Here the approximation $P_e = P_v$ is used because

this is a very small correction and they are close. Hence,

$$\partial B / \partial \phi_2 = (-1/3) (-1) \partial / \partial \phi_2 P_L/P_e$$

$$= (1/3) P_L \partial / \partial \phi_2 1/P_e \text{ and this vanishes too.}$$

4. $\delta = 1 - d_G/d + 0.5 (d_G/d)^2$ and $d_G = P_e MW_1/RT_1$,

ideal gas and T_1 and ϕ_2 are orthogonal. With a little algebra and using the previous

results it is readily seen that $\partial \delta / \partial \phi_2$ also vanishes.

Next, examining Eqs. (16) and (18) on page 129 we realize that:

$$\partial \phi_2 = (d_1/d_2) \partial w_2$$

The solvent and polymer are incompressible, so d_1 and d_2 are taken as constant.

Finally, using the fact that the four differential quantities are zero gives:

$\lim_{w_2 \rightarrow 0} \partial \ln A / \partial w_2 = (1/2\sigma) (\partial \sigma / \partial w_2)$ and simultaneously,

$$\lim_{w_2 \rightarrow 0} \partial K / \partial w_2 = -1.182 \times 10^5 (3\sigma)^2 (\partial \sigma / \partial w_2) / (T(P_e - P_L)^2 \delta^2)$$

Therefore, their ratio becomes:

$$\lim_{w_2 \rightarrow 0} (\partial \ln A / \partial w_2) / (\partial K / \partial w_2) = 1/(6K)$$

This is all only as polymer concentration approaches zero, or pure liquid.

So, we have the starting equation with an integration constant that was

calculated for seven different low molecular weight solvents.

$$d \ln A / dK = 1/(6K) \quad [\text{nomenclature omitted}]$$

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