Elimination of the Prefactor and a New Equation in Classical Nucleation Theory

John H. Jennings^{1*}

DOI: 10.9734/bpi/cpcs/v6

ABSTRACT

In 2020, Jennings found a way to take the nucleation rate for liquid→gas, according to BLANDER/KATZ $J=A\exp K$, to $J=f(K)$ in an exact theory, and K was evaluated exactly among the first two of the three papers in this chapter.

The third paper gives the new proposed equation for the limit of superheat by addition of electrolyte because of a pattern. We see the pattern in the equations arising from the CLAUSIUS-CLAPEYRON relation (thermodynamics – boiling point elevation) and PRIGOGINE/MARECHAL (statistical mechanics – limit of superheat).

Keywords: Homogeneous nucleation; polymer solutions; Classical Nucleation Theory.

1. PART 1: A NEW CONSTANT FROM CLASSICAL NUCLEATION THEORY

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 . $K = -64.5605$.

Keywords: Homogeneous nucleation; Flory-Huggins theory; limit of superheat; differential equation; polymer solutions.

NOMENCLATURE

a	: surface area of solvent molecule
A	: prefactor
B	: parameter
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

¹Jennings Research and Editing, 2530 Hillegass Ave. #307 Berkeley, CA 94704, USA.

*Corresponding author: E-mail: jennings.333.jhj@gmail.com;

Pe : equilibrium vapor pressure
PL : 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

1.1 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 [1-6].

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 [6-12].

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.

$$\Delta T = 3kT^2 wMW1/\sigma aMW2 \quad (1)$$

Blander and Katz's (15) is the abbreviated formula (2) here for the nucleation rate, J, discussed in Appendix 1.1.

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

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 1.2 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.

1.2 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 1.2. 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 Shiau 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 1.2. 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.

1.3 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.

1.3.1 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 1.1 and APPENDIX 1.2, 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 1.1 for Blander and Katz's exact expression for J and details on the workup of the data. See Appendix 1.2 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 = 10⁴ – 10⁶) 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.

$$1830.84 = T (Pe - PL)^{\frac{2}{3}} \delta^2 / \sigma^3 \quad (6)$$

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.

1.4 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 prefactor in classical nucleation theory for liquid-->gas has been eliminated and K has been evaluated exactly for all solvents.

DISCLAIMER

This article is adapted from Jennings, J. H. (2019). Eliminating the Pre-exponential Factor in Classical Nucleation Theory. Chemical Science International Journal, 28(3), 1-6. <https://doi.org/10.9734/CSJI/2019/v28i330140>

REFERENCES

1. CRC Handbook for Chemistry and Physics 66th Ed.
2. Iran website for Antoine Equation constants
Available: http://teachers.iauo.ac.ir/images/Uploaded_files/ANTOINE_COEFFICIENTS_FOR_VAPOR_PRESSURE%5B1%5D%5B4619259%5D.PDF
3. Various Internet websites for solvent densities.
4. Blander M, Katz JL. Bubble Nucleation in Liquids. AIChE J. 1975;21(5):833-848.
5. Bovey FA, Winslow FH. Macromolecules: An Introduction to Polymer Science. Academic Press; 1979.
6. Jasper JJ. The surface tension of pure liquid compounds. J Phys Chem Ref Data. 1972;1: 841-1009.
7. Jennings JH. Eliminating the pre-exponential factor in classical nucleation theory. Chemical Science International Journal. 2019;28(3):1-6.
8. Jennings JH. Homogeneous nucleation from polymer solutions. Polymers Research J. 2014; 8(4):311-319.
9. Jennings JH. Limit of superheat of polystyrene-cyclohexane solutions: Theory. Int. J. Thermodynamics. 2012;15(3):127-132.

10. Jennings JH, Middleman S. Homogeneous nucleation of vapor from polymer solutions. *Macromol.* 1985;18:2274-2276.
11. Shiau L. The temperature dependence of the pre-exponential factor and interfacial energy for aqueous glycine solutions based on the metastable zone width data. *J. Crystal Growth.* 2018; 496-497:18-23.
12. Siow KS, Patterson D. Surface thermodynamics of polymer solutions. *J. Phys. Chem.* 1973; 77(3):356-365.

APPENDIX 1.1

$$1) J = A \exp K$$

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

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 prefactor, 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 1.2

Proof of $\ln A/dK = 1/(6K)$ for all pure liquids $J = A \exp K$ from Blander and Katz classical nucleation theory liquid→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. [9]. page 127-128.

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

$$(\sigma - \sigma_1) a / kT = \ln (\phi_{1S} / \phi_1) + ((r - 1) / r) (\phi_{2S} - \phi_2) \quad (A)$$

$$\ln[(\phi_{2S} / \phi_2)^{1/r} / (\phi_{1S} / \phi_1)] = (\sigma_1 - \sigma_2) a / kT \quad (B)$$

Now, near $\phi_2 = 0$, Eq. (B) becomes

$$\phi_{2S} = \phi_2 \exp [r (\sigma_1 - \sigma_2) a / kT]$$

Putting in the numbers, $\partial\phi_{2S}/\partial\phi_2 \approx 10^{-38}$ for $MW_2 = 2000$, $r = 13.4$ and even less for higher MW.

First, it is necessary to prove Eq. (11) in Ref. [9].

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

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

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.

$$K = -1.182 \times 10^5 \sigma^3 / (T (P_V - P_L)^2) = -1.182 \times 10^5 \sigma^3 / (T (P_e - P_L)^2 \delta^2)$$

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

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

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

We prove these four differentials are zero, which simplifies it, page 128 of Ref. [9].

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

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

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

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

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

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

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

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

ideal gas and T_l 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 of Ref. [9] 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:

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

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

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.

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

2. PART 2: CLASSICAL NUCLEATION AND LATTICE MODEL UNITE

ABSTRACT

Classical nucleation theory predicts the limit of superheat of liquids quite well. To come up with an equation for the limit of superheat of polymer solutions, the lattice model for polymer solutions was used to give the surface tension of polymer solutions. A formula for bubble nucleation in polymer solutions was derived by Jennings with the precursor equation $d \ln A / dK = 1/(6K)$ where $J = A \exp K$ gives the nucleation rate for liquids. The aim of this paper was to show that the precursor equation holds for monomer in the polystyrene-cyclohexane system. Thus, the precursor equation is true for all molecular weight polymer. This happens because the surface tension of polystyrene is significantly more than cyclohexane and the influence of the surface tension dominates.

Keywords: Polymer solutions; classical nucleation theory; surface tension; limit of superheat; lattice model.

NOMENCLATURE

a : Surface area of solvent molecule
 A : Prefactor
 B : Parameter
 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 of limit of superheat of solution
 T_o : Limit of superheat of solvent in Kelvin
 w : Weight fraction polymer
 δ : Poynting correction factor
 ΔT : Rise in superheat in Centigrade = $T - T_o$
 σ : Surface tension

2.1 INTRODUCTION

Classical nucleation theory goes back to Josiah Willard Gibbs where increasing entropy and decreasing energy give way to an emerging bubble forming aided by the rise in temperature known as the limit of superheat. Flory and Huggins theory provided an understanding of the behavior of a polymer solution and Prigogine and Marechal [1] derived equations for the surface tension of polymer solutions, following Flory/Huggins. Other attempts at solving the problem of bubble nucleation in polymer solutions were complicated and had no good data, for example (in addition to Prud'homme/Gregory [2]), Yarin et al. [3] said bubble growth is controlled by momentum transfer and diffusion or Han and Han [4] did a lengthy theoretical study that was very involved. My theory offers simple equations that are exact and predict the linearity in weight fraction and the trend in molecular weight polymer. Conceivably, the equations and results in this study could be applied toward fuel burning where the limit of superheat is present and affects the efficiency of thrust of a rocket or high performance racecar or a new way of measuring polymer molecular weight.

2.2 THEORY

This paper is based on a highly cited paper by Blander and Katz [5] and another paper by Siow and Patterson [6]. Jennings joined these streams of thought for the first time in 2012 by coming up with this formula for the limit of superheat as polymer $\rightarrow 0$.

$$\lim_{w_2 \rightarrow 0} \partial T / \partial w_2 = (MW_1 / MW_2) (3kT_o^2 / \sigma a) \quad (1)$$

Mathematically, Eq. (1) is only true in the limit of zero weight fraction polymer in the solution because of the limitation in getting the surface tension. However, the actual Jennings and Middleman [7] data shows straight vectors in (w,T) space for lower molecular weight. In Jennings' [8] paper, the [9] equation (1) was expanded because of that. Here is the expanded equation.

$$\Delta T = 3kT_o^2 w MW_1 / \sigma a MW_2 \quad (2)$$

So, the question is, what led to Eq. (2)? It is Eq. (3) from Jennings [9] paper.

$$\lim_{w_2 \rightarrow 0} (\partial \ln A / \partial w_2) / (\partial K / \partial w_2) = 1 / (6K) \quad (3)$$

Another way to write (3) is (4).

$$d \ln A / dK = 1 / (6K) \quad (4)$$

A and K are found in the equation (Z) in the APPENDIX 2.1, Blander and Katz's formula for bubble nucleation in liquids: A is the prefactor in (Z) and K is the exponent in (Z). In APPENDIX 2.1 is sketched out my method for checking the validity of (4) for monomer, that is $r = 1$, where r is the ratio of the molar volume of polymer to the molar volume of solvent. Furthermore, (4) has a well-defined integration constant that was calculated in Jennings [10] article. See the same Jennings [10] article for details pertaining to this derivation and Jennings [9] for all of the values to input in the equations in

APPENDIX 2.1. Polystyrene-cyclohexane is a model system, so Eq. (4) is proposed as a general equation when the surface tension of the polymer is significantly greater than the surface tension of the solvent.

2.3 METHODOLOGY

In the early 1980s, Jennings and Middleman collected data on liquid→gas nucleation in polymer solutions that was published in 1985. In early 2020 the study was complete, except direct calculation revealed that the surface tension is so influential that only the surface tension terms matter and so the 2012 equations are true for any degree of polymerization, that is $r = 1$ up to $r = \text{infinity}$, for the polystyrene-cyclohexane model system.

2.4 RESULTS AND DISCUSSION

Unfortunately, there is no known data, except a lone styrene point in the 1985 paper, and plugging in the numbers gave a result that was off by about a factor of 10. There is data on polystyrene/benzene gathered by Prud'homme and Gregory [2], but it does not agree with Eq. (2) at all. The beauty of this entire study from Fall 1980 to now is that it shows how the very successful classical nucleation theory unites with the lattice model for polymer solutions. The author knows of no one else who used Siow and Patterson's [6] theory to solve this problem and all of the others who attempted it had complicated equations.

2.5 CONCLUSIONS

The author first started on this project in 1980 and feels that this paper advances it. It is remarkable how influential the surface tension is in bubble nucleation. Possibly this paper will get noticed and lead others to explore the ramifications of what started with Gibbs and Flory/Huggins.

ACKNOWLEDGEMENTS

Newman Hall, a Catholic Church near the author, has been a source of inspiration. This paper is dedicated to Father Ivan Tou of Newman Hall, who is the pastor there. May the Virgin Mary intercede for us.

REFERENCES

1. Prigogine I, Marechal J. The influence of differences in molecular size on the surface tension of solutions IV. J. Coll. Sci. 1952;7:122-127.
2. Prud'homme RK, Gregory WJ. Homogeneous nucleation temperatures for concentrated polystyrene-benzene solutions. J. Polym. Sci. Symp. 1985;72:263-275.
3. Yarin AL, Lastochkin D, Talmon Y, Tadmor Z. Bubble nucleation during devolatilization of polymer melts. AIChE J. 1999;45:2590-2605.
4. Han JH, Han CD. Bubble nucleation in polymeric liquids. II. Theoretical Considerations. J. Polym. Sci. Part B. 1990;28:743-761.
5. Blander M, Katz JL. Bubble nucleation in liquids. AIChE J. 1975;21(5):833-848.
6. Siow KS, Patterson D. Surface thermodynamics of polymer solutions. J. Phys. Chem. 1973;77(3):356-365.
7. Jennings JH, Middleman S. Homogeneous nucleation of vapor from polymer solutions. Macromol. 1985;18:2274-2276.
8. Jennings JH. Homogeneous nucleation from polymer solutions. Polymers Research J. 2014;8(4):311-319.
9. Jennings JH. Limit of superheat of polystyrene-cyclohexane solutions: Theory. Int. J. Thermodynamics. 2012;15(3):127-132.
10. Jennings JH. A new constant from classical nucleation theory. IAJER. 2020;3(1):1-6.

APPENDIX 2.1

Part 1

Here, we establish $\ln A/dK=1/(6K)$ for $r = 1$.

This is the Proof of $\ln A/dK = 1/(6K)$ for all pure liquids $J = A \exp K$, where

J = nucleation rate, A = prefactor and K = exponent.

from Blander and Katz classical nucleation theory liquid→gas. Siow and Patterson present equations for the surface tension of polymer solutions.

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 2012.

page 127-128. Everything here is done as $\phi_2 \rightarrow 0$ and $T \rightarrow T_0$.

Note that ϕ_2 and T are orthogonal.

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

$$(\sigma - \sigma_1) a / kT = \ln (\phi_{1S} / \phi_1) + ((r - 1) / r) (\phi_{2S} - \phi_2) \quad (A)$$

$$\ln[(\phi_{2S} / \phi_2)^{1/r} / (\phi_{1S} / \phi_1)] = (\sigma_1 - \sigma_2) a / kT \quad (B)$$

Now, near $\phi_2 = 0$, Eq. (B) becomes

$$\phi_{2S} = \phi_2 \exp [r (\sigma_1 - \sigma_2) a / kT]$$

Putting in the numbers for polystyrene-cyclohexane, $\partial \phi_{2S} / \partial \phi_2 \approx 10^{-38}$ for $MW_2 = 2000$, $r = 13.4$, and even less for higher MW. The object here is to let $r = 1$ near $\phi_2 = 0$ and T near T_0 .

Thus $\phi_{2S} = \phi_2 \exp [(\sigma_1 - \sigma_2) a / kT]$ and so $(\partial \phi_{2S} / \partial \phi_2) = \exp [(\sigma_1 - \sigma_2) a / kT]$.

All of the details had to be included because it was only evident later that the surface tension term dominated. This had to be shown by direct calculation.

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

$$\partial d / \partial \phi_2 = (d_2 - d_1) (\partial \phi_{2S} / \partial \phi_2) = (d_2 - d_1) \exp [(\sigma_1 - \sigma_2) a / kT_0]$$

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

$$\partial P_e / \partial \phi_2 = - P_e(0) (\partial \phi_{2S} / \partial \phi_2) = - P_e(0) \exp [(\sigma_1 - \sigma_2) a / kT_0]$$

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,

$$\partial B / \partial \varphi_2 = (-1/3) (-1) \partial / \partial \varphi_2 P_L / P_e$$

$$= (1/3) P_L \partial / \partial \varphi_2 1 / P_e \text{ and } = (1/3) P_L / P_e(0) \exp [(\sigma_1 - \sigma_2) a / kT_0]$$

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

$$d_G / d = x \text{ is small so } \delta \approx e^{-x}$$

After some manipulation we have.

$$\partial \delta / \partial \varphi_2 = \delta [d_G / d + (d_G / d)^2 (d_2 - d_1)] \exp [(\sigma_1 - \sigma_2) a / kT_0]$$

Note ideal gas and T and φ_2 are orthogonal. These differentials don't vanish.

It was seen that the surface tension influence dominates wherever it occurs.

$\partial \varphi_2 / \partial \varphi_2 \approx$ only vanishes with r greater than 5, say.

To avoid clutter, the values for all these unknowns are left out and they are all in Jennings 2012.

International Journal of Thermodynamics article. This part is to establish the method.

Now, we get $\lim_{\varphi_2 \rightarrow 0} \partial \sigma / \partial \varphi_2 = (k T_0 / a) (1 - \exp [(\sigma_1 - \sigma_2) a / kT_0]) = (k T_0 / a) (0.9984)$.

This is arrived at by letting r = 1 in (A) above and partial differentiating with respect to φ_2 .

It is then seen that the surface tension terms dominate for all r, so $d \ln A / dK = 1/6K$.

σ_2 is significantly larger than σ_1 for this model system (polystyrene-cyclohexane).

Part 2

Getting all these quantities is the hard part and the rest is calculating

$\lim_{\varphi_2 \rightarrow 0} (\partial \ln A / \partial \varphi_2) / (\partial K / \partial \varphi_2) = 1/(6K)$, where A/K are the prefactor/exponent in (Z) above.

For r = 1, $1/(6K) = -0.002399$, or K = -69.47.

From the IAJER article (PART 1) by Jennings 2020, r = 13.4 and K = -64.56 for 10 solvents, polar & non-polar.

Deriving Jennings 2012 Equation (1) in its THEORY section depends on $|1/(6K)|$ being small, so we have shown here it is true for r = 1 to r = infinity. The surface tension dominates, as is noted by Blander and Katz 1975. The validity of $d \ln A / dK = 1/(6K)$ is therefore true for all r in the polystyrene-cyclohexane system and its integration constant for non-polar and polar solvents was calculated in Jennings' IAJER 2020 PART 1 article. All of this puts Jennings' 2014 Polymers Research Journal equation on solid ground, which is formula (2) in this paper, the equation for bubble nucleation in polymer solutions. The polymer solution data for this was first published by Jennings/Middleman 1985 MACROMOLECULES for polystyrene-cyclohexane.

3. PART 3: THE EQUATION FOR RISE IN SUPERHEAT BY ADDING ELECTROLYTE

ABSTRACT

For many liquids, the limit of superheat is $0.89 T_c$, where T_c = temperature Kelvin at critical point. The rise in the limit of superheat by addition of polymer has a formula, B' , derived by Jennings, and this paper makes use of a pattern to predict the formula for rise in superheat by adding electrolyte, B . The equations for boiling point elevation by addition of electrolyte, A , and polymer, A' , are known, so we make use of a proportion and solve for the unknown, B , thus: $B = (A/A') \times B'$ to get the equation.

A , A' and B' all have the phase change temperature squared at 1 atmosphere pressure in the numerator times the ratio of the molecular weight solvent divided by the product of the density of solvent times molecular weight solute in the expression that equals $\lim_{c \rightarrow 0} (dT/dc)$ giving the limiting slope of rise in temperature versus concentration solute. The van't Hoff factor is included. The proposed formula B for RISE IN SUPERHEAT BY ADDITION OF ELECTROLYTE is:

$$\lim_{c \rightarrow 0} (dT/dc)_s, \text{ electrolyte} = (3 k MW_1 T_s^2 i) / (\rho_1 \sigma_1 a MW_2(e)).$$

Keywords: *Homogeneous nucleation; boiling point elevation; limit of superheat; polymer solution; electrolyte solution.*

NOMENCLATURE

a	: Surface area of solvent molecule at T_s
A	: Equation for boiling point elevation by adding electrolyte
A'	: Equation for boiling point elevation by adding polymer
B	: Equation for rise in superheat by adding electrolyte
B'	: Equation for rise in superheat by adding polymer
c	: Concentration of solute = m^2/V
$c \rightarrow 0 (dT/dc)$	: limiting slope for infinite dilution
i	: Van't Hoff factor (equals $Z^+ + Z^-$ for numbers of + or – ions)
k	: Boltzmann constant
m	: Molality
m_i	: Mass: 1, solvent; 2, solute
MW_1	: Molecular weight of solvent
$MW_2(e)$	: Molecular weight of electrolyte
$MW_2(p)$	: Molecular weight of polymer
R	: Universal gas constant
T	: Temperature Kelvin of solution
T_c	: Critical temperature of solvent Kelvin
T_i	: Temperature Kelvin, b = boiling, s = superheat
V	: Volume of a sample of solution
w_2	: Weight fraction polymer
ΔH_{vap}	: Heat of vaporization of solvent per mole
ΔT	: Incremental rise in boiling or superheat = $T - T_i$
ρ_1	: Density of pure solvent at phase-change temperature = m_1/V
σ_1	: Surface tension of pure solvent at limit of superheat

3.1 INTRODUCTION

The equation for boiling point elevation is arrived at by combining the Clausius-Clapeyron equation with Raoult's law at infinite dilution, where the molar heat of vaporization appears in the denominator for $c \rightarrow 0 (dT/dc)$ and it has been presented for electrolyte Wall [1] and Blackmore [2]. Jennings [3] derived the formula for infinite dilution for the limit of superheat by adding polymer. By taking the proportion $A/A' = B/B'$ because of a pattern between the equations, we form $B = (A/A') \times B'$ for the desired equation. This appears to give a sensible answer. Work toward Jennings [3] began in 1980 with a project on Bubble Nucleation in Polymer Solutions, where the data was published by Jennings and Middleman [4].

3.2 THEORY

The formula for boiling point elevation by addition of electrolyte is presented (1) in Wall [1], page 363, and (2) is conversion of concentration to molality. In addition, the heat of vaporization, ΔH_{vap} , is per mole.

$$\Delta T = (MW_1 R T_b^2 m) / (1,000 \Delta H_{vap}) \quad (1)$$

$$m = (1,000 c) / (\rho_1 MW_2(e)) \quad (2)$$

Putting (2) into (1), we have, adding the van't Hoff factor, $i = Z^+ + Z^-$ for ions.

$$\lim_{c \rightarrow 0} (dT/dc)_b, \text{ electrolyte} = (R T_b^2 MW_1 i) / (\rho_1 \Delta H_{vap} MW_2(e)) \quad (3)$$

Equation (3) is equation A in the ABSTRACT.

The formula for boiling point elevation by addition of polymer is presented in BLACKMORE [2].

$$\lim_{c \rightarrow 0} (dT/dc)_b, \text{ polymer} = (R T_b^2 MW_1) / (\rho_1 \Delta H_{vap} MW_2(p)) \quad (4)$$

Equation (4) is equation A' in the ABSTRACT. Notice the $MW_2(p)$, where p is for polymer instead of e for electrolyte.

The formula for limit of superheat by addition of polymer was derived by Jennings [3] and is:

$$\lim_{w_2 \rightarrow 0} (dT/dw_2)_s, \text{ polymer} = (3 k T_s^2 MW_1) / (\sigma_1 a MW_2(p)) \quad (5)$$

Notice that σ is in the denominator instead of ΔH_{vap} . We need to convert from w_2 , weight fraction at infinite dilution to concentration at infinite dilution.

$$w_2 = m_2 / (m_1 + m_2) \quad (6)$$

$$\lim_{m_2 \rightarrow 0} w_2 = m_2/m_1 \quad (7)$$

$$(dT/dw_2) = (dT/dc) (dc/dw_2) \quad (8)$$

$$\rho_1 = m_1/V \text{ independent of } \lim_{m_2 \rightarrow 0} w_2 \quad (9)$$

$$(dc/dw_2) = (d(m_2/V) / d((m_2/V)/(m_1/V))) \quad (10)$$

$$(dc/dw_2) = m_1/V \quad (11)$$

Because $c = m_2/V$, we have Jennings formula in terms of concentration.

$$\lim_{c \rightarrow 0} (dT/dc)_s, \text{ polymer} = (3 k T_s^2 MW_1) / (\rho_1 \sigma_1 a MW_2(p)) \quad (12)$$

Equation (12) is equation B' in ABSTRACT. $B = (A/A') \times B'$ to get proposed formula.

Proposed formula B for RISE IN SUPERHEAT BY ADDITION OF ELECTROLYTE is then:

$$\lim_{c \rightarrow 0} (dT/dc)_s, \text{ electrolyte} = (3 k T_s^2 MW_1 i) / (\rho_1 \sigma_1 a MW_2(e)) \quad (13)$$

This is because a number of terms cancel out.

3.3 METHODOLOGY

In theory, we saw that the polymer $MW_2(p)$ cancels out, and it should be noted that Jennings [3] theory goes back to Prigogine/Marechal [5], which gives the surface tension for polymer solutions.

The old theory for boiling point elevation for electrolyte is based on small molecules, but BLACKMORE [2] presents it for polymer. There is a kind of corresponding states between boiling point elevation and limit of superheat. All four equations have a similar form.

3.4 RESULTS AND DISCUSSION

One may ask, what is this all good for? A very accurate thermometer is required to measure boiling point elevation, but in Jennings [3] experiment, the effect was 10-15 degrees centigrade rather than millidegrees. Supposedly this is a better way to measure the molecular weight of a polymer, but an apparatus measuring the limit of superheat is rather complex.

3.5 CONCLUSION

Physical chemistry has a beauty and symmetry all its own. This paper completes the search for the missing formula – RISE IN SUPERHEAT BY ADDITION OF ELECTROLYTE. It takes more study to find a use for experiments above the limit of superheat of liquids.

ACKNOWLEDGEMENT

For my part, I'd like to first thank family, who has supported me in pursuit of science. I name my brother Charles Jennings, my cousin Ellen Haugen, and a cousin's husband, Tony Davies. For friends, in the same way, I name Mark Jones, Therese Pipe, Ellen Farrell, Kelly Moy, and Stephen Ternullo. All of these encouraged and supported me in their own way.

First, I'm thankful for the computer expertise of my friend Bob Guiang. Second, I'm thankful for the financial support of the United States Social Security Administration.

DISCLAIMER

This chapter for Book Publisher International is the sequel to a previous chapter published by Nova Science Publishers in 2014. The Nova chapter is entitled, A New Equation for Homogeneous Nucleation from Polystyrene Solutions IN Polystyrene: Synthesis, Characteristics and Applications. Editor Cole Lynwood ISBN 978-1-63321-356-2

COMPETING INTERESTS

Author has declared that no competing interests exist.

REFERENCES

1. Wall, Frederick T. Chemical thermodynamics: A course of study, 2nd Ed. WH Freeman and Co; 1965.
2. Blackmore WR. Ebulliometry and the determination of the molecular weights of polymers. Can. J. Chem. 1959;37:1508-1516.
3. Jennings JH. Limit of superheat of polystyrene-cyclohexane solutions: Theory. Int. J. Thermodynamics. 2012;15(3):127-132.
4. Jennings JH, Middleman S. Homogeneous nucleation of vapor from polymer solutions. Macromol. 1985;18:2274-2276.
5. Prigogine I, Marechal J. The Influence of differences in molecular size on the surface tension of solutions IV. J. Coll. Sci. 1952;7(2):122-127.

Biography of author(s)

John H. Jennings

Jennings Research and Editing, 2530 Hillegass Ave. #307 Berkeley, CA 94704, USA.

He was born into the USA educated Auchincloss family and his father, Percy H. Jennings, Jr., M.D. was a prominent physician in Berkeley, California. In 1973, he graduated from UC Berkeley with Distinction in General Scholarship in Chemistry. In 1980 at UCSD, he started studying BUBBLE NUCLEATION IN POLYMER SOLUTIONS, a topic he pursued until 2020. Stanley Middleman was Principal Investigator while he was at UCSD. His studies on the topic resulted in finding out data and deriving theory that gave the total solution, solidly establishing this formula as describing the rise in superheat by adding polymer. $\Delta T = 3kT^2\omega MW_1/\sigma a MW_2$. This formula is an exact one, with no adjustable parameters, and papers going from 1985 to 2020 give the details proving it. In addition to his physical chemistry studies, he also published two articles in mathematical biology. He earned the Master's in Chemistry at UCSD and enjoys walking, studying topics in science, movies and writing letters. He is a Catholic convert and looks forward to the life to come. He speculates that the above equation has a bearing on fuel injection in high-performance race cars, allowing the temperature of a solution to rise to a realm where the viscosity lowers or is a new way of measuring the molecular weight of polymer.

© Copyright (2020): Author(s). The licensee is the publisher (Book Publisher International).

DISCLAIMER

Part 1 of this chapter is an extended version of the article published by the same author(s) in the following journal. International Advance Journal of Engineering Research (IAJER), 3(1): 01-06, 2020.

Part 2 of this chapter is an extended version of the article published by the same author(s) in the following journal. Chemical Science International Journal, 29(4): 32-36, 2020.

Reviewers' Information

- (1) Harishchander Anandaram, Sri Krishna Arts and Science College, India.
- (2) Oyelakin K. Akinloye, Federal University of Technology, Nigeria.

Part 3 of this chapter is an extended version of the article published by the same author(s) in the following journal. Chemical Science International Journal, 29(6): 19-21, 2020.

Reviewers' Information

- (1) Saba Beg, Aligarh Muslim University, India.
- (2) Ravindra Baburao Talware, Savitribai Phule, Pune University, India.