



# Eliminating the Pre-exponential Factor in Classical Nucleation Theory

**John H. Jennings<sup>1\*</sup>**

<sup>1</sup>*Jennings Research and Editing, 2530 Hillegass Ave. #307 Berkeley, CA 94704, USA.*

## **Author's contribution**

*The sole author designed, analysed, interpreted and prepared the manuscript.*

## **Article Information**

DOI: 10.9734/CSJI/2019/v28i330140

### Editor(s):

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Complete Peer review History: <http://www.sdiarticle4.com/review-history/52902>

**Original Research Article**

**Received 19 September 2019**

**Accepted 27 November 2019**

**Published 05 December 2019**

## **ABSTRACT**

Blander and Katz give a formula in classical nucleation theory,  $J = A \exp K$ , for homogeneous nucleation (liquid $\rightarrow$ gas). Jennings proved that  $d \ln A / dK = 1/6K$  for all pure liquids by combining two theories, taking the limit as polymer concentration $\rightarrow$ 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 7 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.  $C = 74.77 \pm 0.33$  for the 7 solvents (not all alkanes). This eliminates the prefactor A, streamlining J:  $\ln J = (1/12) \ln(K^2) + 74.77 + K$  is the exact new equation. A computer can more easily be used to calculate J, the nucleation rate.

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

\*Corresponding author: E-mail: [jennings.333.jhj@gmail.com](mailto:jennings.333.jhj@gmail.com);

## NOMENCLATURES

$a$	: 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;
$\delta$	: Poynting correction factor;
$\Delta T$	: Rise in superheat in Centigrade;
$\sigma$	: Surface tension;

## 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.

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.

## 2. THEORY

Later on, these two trains of thought developed into 1) modern classical nucleation theory (CNT) as put forth by Blander and Katz [1] and 2) the model for surface tension of polymer solutions (STPS) refined by Siow and Patterson [2]. In 2012, Jennings combined the CNT/STPS equations and that later led to equation (19) in Jennings [3], here as (1), a general formula for bubble nucleation in polymer solutions. The data for (1) are presented in graphical form in Jennings and Middleman [4].

$$\Delta T = 3kT^2wMW_1/\sigma aMW_2 \quad (1)$$

Blander and Katz's (15) is the abbreviated formula (2) here for the nucleation rate,  $J$ , discussed in Appendix 1.

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

Jennings [5], 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 7 fluids, as equation (3) is general.

## 3. 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' [5] 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 Shiau [6], where the temperature dependence of the PEF was investigated. Eq. (3) is the precursor to Eq. (1). Bovey and Winslow [7] 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 [5].

## 4. 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 seven 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.

Notice there is little scatter,  $C = 74.77 \pm 0.33$ . Some of the solvents are alkanes and others are not. It appears that C is a constant for low MW solvents.

Amazingly, this investigation actually ELIMINATES the prefactor A and streamlines Blander/Katz's formula for CNT. In J becomes simply:

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.

Solvent	C	Data	
		Superheat limit (Kelvin)	Molecular weight (g/mol)
cyclohexane	74.82	492.75	84.16
hexane	74.60	457.15	86.18
carbon tetrachloride	74.79	495.06	153.82
pentane	74.84	420.95	72.15
cyclopentane	75.11	456.95	70.14
heptane	74.10	487.15	100.21
benzene	75.14	498.45	78.12

$$\ln J = (1/12)\ln(K^2) + 74.77 + K \quad (5)$$

Since here, the nucleation rate J is solely a function of K, a computer can more easily calculate the nucleation rate.

## 5. 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, so this study is not concerned with calculation of the nucleation rate, but it is shown here that the prefactor in classical nucleation theory for liquid-->gas has been eliminated.

## ACKNOWLEDGEMENTS

This paper is dedicated to my mother, Loretta M. Jennings, who passed away in late 1998. My mom was the mother of four boys and was dedicated to giving us good nutrition. When I was young, she got me tutors and music teachers.

## COMPETING INTERESTS

Author has declared that no competing interests exist.

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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,  $\delta$ , where

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

B is close to 2/3.  $\delta$  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);  $\sigma$  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 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), (B) and (C).

See JH Jennings, International Journal of Thermodynamics article, Ref. (5). 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

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

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. (5).

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

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

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;  $\delta$  is the Poynting correction factor.

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

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

We prove these four differentials are zero, which simplifies it, page 128 of Ref. (5).

$\partial \delta / \partial \phi_2 = 0$ ,  $\partial d / \partial \phi_2 = 0$ ,  $\partial P_e / \partial \phi_2 = 0$ , 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,

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

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

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

ideal gas and  $T_1$  and  $\phi_2$  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:

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

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

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.

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

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