On the Thermodynamics of Nucleation in Weak Gas-Liquid Solutions

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Summary

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Motivation

- A better comprehension of Bubble Nucleation

$$\text{rate} = C[(P_{\text{in}} - P)/\gamma^{1/2}]\exp(-\Delta g^*/kT)$$

$$\text{rate} = [(P_{\text{in}} - P)/199](70/\gamma)^{1/2}\exp\{[-\Delta g^*(P_{\text{in}}, P, \gamma) + \Delta g^*(200, 1, 70)]/310k\}$$

Article's Proposal

- Experiments has shown that the amount of gas dissolved strongly affects the Nucleation;

- Bubble Nucleation takes more time to initiate if there is less solute;

- During a initial period the nucleation is the principal mean to remove excess of solute;

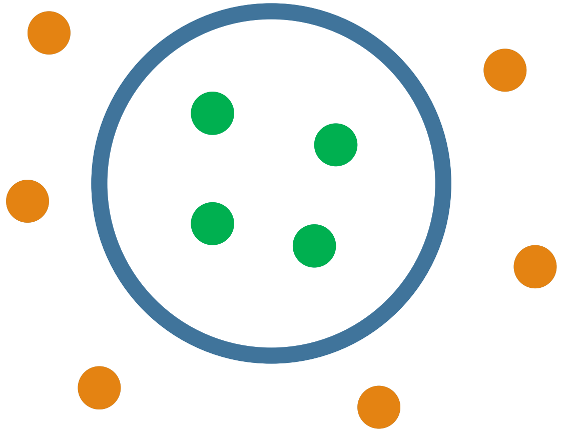
- Main Goal: A theoretical description of the formation of gas-vapor nuclei in a liquid-gas Solution.

The Critical Radius

$\boldsymbol{N'}$

$\boldsymbol{N''}$

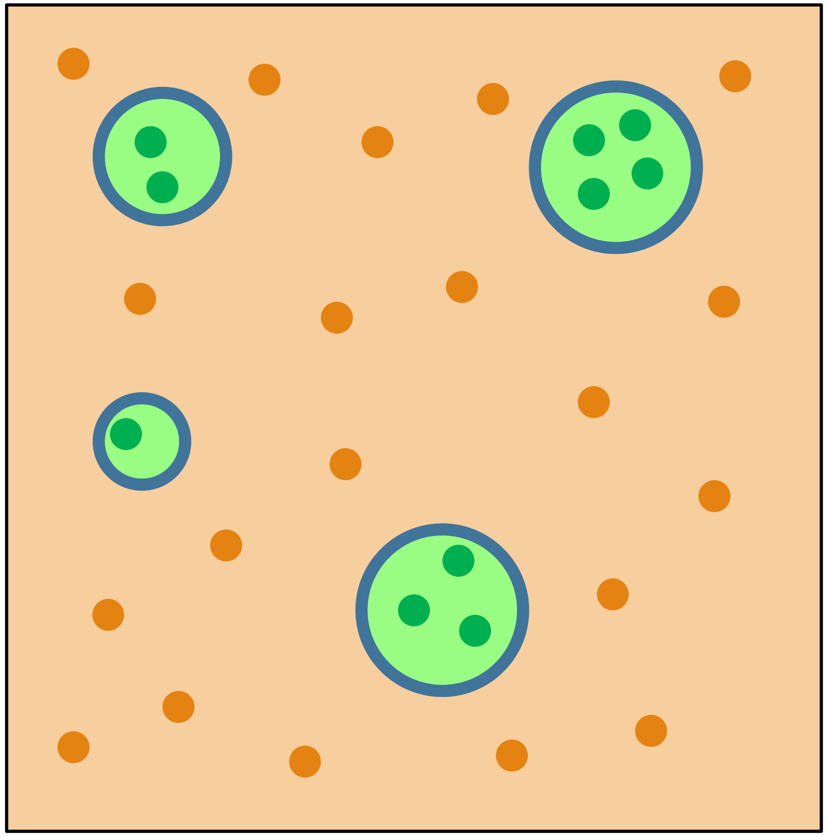
$\boldsymbol{N^{\sigma}}$



$$dU = TdS - P'dV' - P''dV'' + \sigma dA + \sum \mu_i' dN_i' + \sum \mu_i'' dN_i'' + \sum \mu_i^{\sigma} dN_i^{\sigma}$$

$$dF = -SdT - P'dV' - P''dV'' + \sigma dA + \sum \mu_i' dN_i' + \sum \mu_i'' dN_i'' + \sum \mu_i^{\sigma} dN_i^{\sigma}$$

The Critical Radius



$$N_i' + N_i'' + N_i^\sigma = N_{i,T}$$

$$V' + V'' = V_T$$

$$\Downarrow$$

$$\mu_i' = \mu_i'' = \mu_i^\sigma$$

$$\boxed{P'' - P' = \frac{2\sigma}{R_c}}$$

The Critical Radius

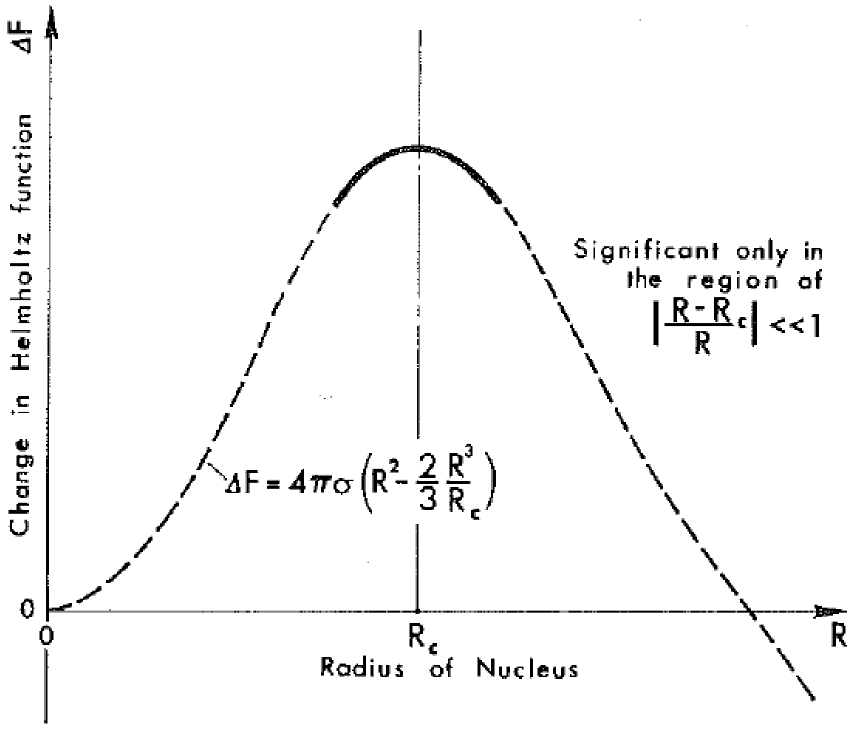


Fig. 1 The behavior of the Helmholtz function in the neighborhood of the critical radius

$$\Delta F = F_B - F_A$$

A: initial system without bubbles
B: system with bubbles

$$F_A = \sum N_i \mu'_{iA} - P_A V$$

$$F_B = F' + F'' + F^{\sigma}$$

$$W_{rev} = \Delta F(R_c) = \frac{4}{3}\pi\sigma R_c^2$$

The Critical Radius

μ_1', μ_2', μ_1'' *and* μ_2'' are now explicit

$+$

$$\mu_1' = \mu_1'' = \mu_1^\sigma$$

$$\mu_2' = \mu_2'' = \mu_2^\sigma$$

$$P'' - P' = \frac{2\sigma}{R_c}$$

$$R_c = \frac{2\sigma}{\frac{\eta P_\infty}{\upsilon_1} + \frac{P'}{\upsilon_2}\frac{c'}{c_0} - P'}$$

P_∞: Saturation pressure of pure liquid;

υ_i: Activity coefficient of component i;

c': Concentration of the gas in liquid phase;

c_0: Concentration of the gas in a liquid saturated with gas across a flat surface;.

Effect of Nonideal Gas Behavior

"Imagine a solution under initial pressure P_I and the concentration of gas is the saturation concentration. Assume that the pressure is suddenly reduced to a pressure P'. What is the critical radius in this second state?"

$$R_c = \frac{2\sigma}{\frac{\eta P_\infty}{\upsilon_1} + \frac{P'}{\upsilon_2}\frac{c'}{c_0} - P'}$$

- Method of Hildebrand and Scott, based on Raoults' law : ideal saturation concentration;
- Method of Kirchevsky and Kasarnovsky, modified Henry's law: nonideal concentration;
- Lewis and Randall rule is used to determinate the activity coefficients;
- There is four possible combinations with ideal/nonideal concentration and ideal/nonideal gas mixture inside the bubble: $R_{II}, R_{IN}, R_{NI}, R_{NN}$;

Effect of Nonideal Gas Behavior

Table 1 Comparison of critical radii for CO_2–water solution at 32 deg C (89.6 deg F) and $P' = 1$ atm

Initial Pr. atm	R_{II} inch × 10^5	R_{IN} inch × 10^5	R_{NN} inch × 10^5	R_{NI} inch × 10^5
2.0	5.1320	5.0799	5.3143	5.3689
3.0	2.5876	2.5616	2.7286	2.7563
4.0	1.7137	–1.6966	1.8422	1.8609
5.0	1.2718	1.2591	1.3944	1.4085
6.0	1.005	0.9950	1.1242	1.1356
7.0	0.8265	0.8182	0.9434	0.9530
8.0	0.6986	0.6916	0.8141	0.8223
9.0	0.6025	0.5965	0.7169	0.7241
10.0	0.5277	0.5224	0.6412	0.6477
11.0	0.4678	0.4631	0.5806	0.5865
12.0	0.4187	0.4145	0.5310	0.5364
13.0	0.3777	0.3740	0.4897	0.4946
14.0	0.3431	0.3397	0.4547	0.4593
15.0	0.3133	0.3102	0.4247	0.4290

Table 2 Comparison of critical radii for nitrogen–water at 32 deg C (89.6 deg F) and $P' = 1$ atm

Initial Pr. atm	R_{II} inch × 10^5	R_{IN} inch × 10^5	R_{NN} inch × 10^5	R_{NI} inch × 10^5
2.0	5.2508	5.2467	5.2727	5.2768
3.0	2.6831	2.6815	2.7018	2.7034
4.0	1.8006	1.7997	1.8179	1.8188
5.0	1.3542	1.3535	1.3707	1.3714
6.0	1.0847	1.0842	1.1007	1.1012
7.0	0.9043	0.9039	0.9200	0.92047
8.0	0.7751	0.7748	0.7906	0.7909
9.0	0.6780	0.6777	0.6934	0.6936
10.0	0.6024	0.6021	0.6176	0.6178
11.0	0.5418	0.5416	0.5570	0.5571
12.0	0.4922	0.4920	0.5072	0.5074
13.0	0.4508	0.4507	0.4658	0.4660
14.0	0.4158	0.4157	0.4307	0.4308
15.0	0.3858	0.3856	0.4006	0.4007

Effect of Nonideal Gas Behavior

- Before we considerate that the concentration of the Solution was the saturation concentration corresponding to P_I. If we calculate the critical radius in function of the saturation concentration of the actual pressure, what happens?

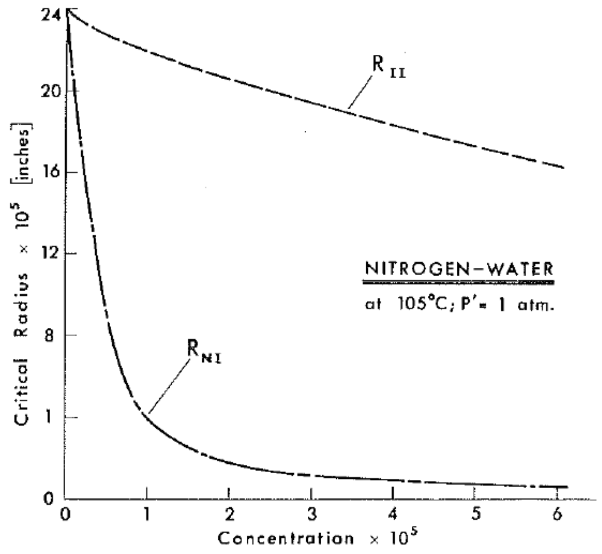


Fig. 2 The critical radius based on the ideal concentration (R_{II}) and on the nonideal concentration (R_{NI}) as a function of the gas concentration in the solution

- The critial radius dependes very strongly on which method is used to predict the saturation concentration;

- The maximum percentage difference that was approximately 4 percent before rises to a difference bigger than an order of magnitude;

Nucleation Pressure

- From statistical Thermodynamics it is known that the probability of a fluctuation occour at any instant in a small part of the system is inversely proportional to na exponential of the reversible work required to produce the change in the thermodynamics properties:

$$Probability = Zexp\left({}^{-W_{rev}}/_{kT}\right)$$

- Surprisingly (or not) a critically sized nucleus is formed by fluctuations in the system, so

$$J = Zexp\left[{}^{-\left(\frac{4}{3}\pi\sigma R_c^2\right)}/_{kT}\right]$$

Nucleation Pressure

- Using the relation

$$\boldsymbol{P'' - P' = \frac{2\sigma}{R_c}}$$

- The rate becomes

$$J = Zexp\left[{}^{-16\pi\sigma^3}\!\big/_{3kT(\boldsymbol{P''} - \boldsymbol{P'})^2}\right]$$

- $\boldsymbol{P'}$ here is the pressure in the liquid, also the Nucleation pressure;
- We can determinate this pressure from the rate J with a “resonable” rate (like one bubble per sec) and for a given temperature or using the generalized Kelvin equation when the gas concentration and saturation concentration are known.

Nucleation Pressure

- They assume that ethyl ether is saturated with nitrogen at a pressure P_I;
  - P_I is the partial pressure of nitrogen above the solution;
  - $P_I = 0$: Pure liquid;

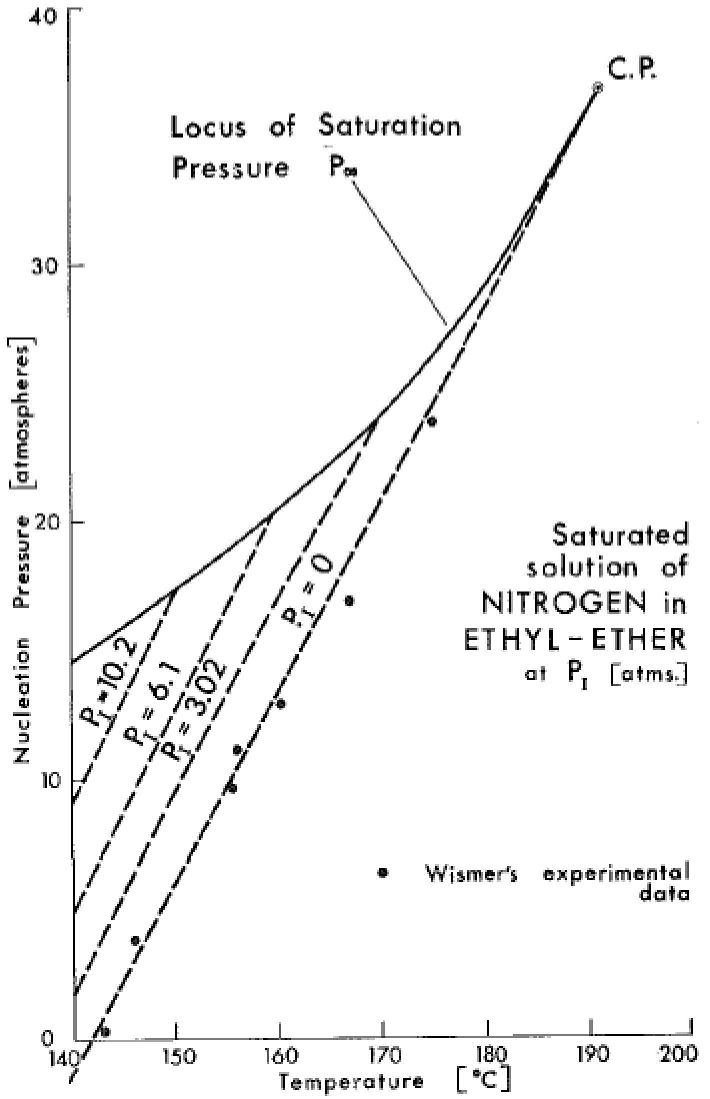


Fig. 3 The pressure and temperature at which nucleation takes place in solutions in which the gas content is equivalent to that of a solution saturated by gas at partial pressure P_I

Conclusion

- The critical radius of a weak solution is less than that of a pure liquid and the internal pressure in the bubble is higher;

- Makes difference in which way we treat the gas, as ideal or nonideal;

- The nucleation has became less foggy (if I can say that) and the article has shown ways to approach the nucleation pressure;

Thank you!