

Int. j. adv. multidisc. res. stud. 2024; 4(1):623-625

Received: 07-12-2023 **Accepted:** 17-01-2024

ISSN: 2583-049X

Mini-Review on Corresponding States

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International Journal of Advanced Multidisciplinary

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Research and Studies

Abstract

In Physical Chemistry it is found that various molecules behave in a parallel way, mathematically speaking. The Van der Waals gas, an improvement on the ideal gas, is a prime example of the principle of corresponding states. Here the author will give the proof for the surface tension formula, another example. Several graphs of this kind are included. Equations of this sort unify molecular properties and show rhe beauty of Physical Chemistry. Einstein's viscosity law gave rise to a curve to calibrate gel permeation chromatogrphy columns and Guggenheim offers a curve that is also an example of corresponding states. From a 1980 Physics thesis, the author discovered an example for homogeneous nucleation of low molecular weight gases. This article touches a few bases on the topic.

Keywords: Corresponding States, Surface Tension, Einstein Viscosity Law, Van Der Waals

Introduction

The prime example of corresponding states is the ideal gas, for dilute gases.

$$PV = nRT$$
(1)

A significant improvement is found in the Van der Waals gas.

$$(P + n^2 a / V^2) (V - n b) = n R T$$
(2)

Where the critical volume, temperature and pressure are the following.

Above the critical temperature there is no longer a meniscus between gas and liquid. The constants a and b are available for many gases. The Van der Waals gas reduces to the ideal gas when the gas is dilute (n / V small). The boiling point, critical point and critical compressibility factor can be derived from the Van der Waals formula. In Discussion 1 and Discussion 2 more examples of the principle of corresponding states will be presented with three graphs at the end.

Discussion 1

At the end of the paper are three graphs showing corresponding states. The author will discuss them here: 1) for calibrating a column for gel permeation chromatography, Einstein's viscosity law ^[1] was used with success, because it is difficult to calculate the hydrodynamic volume, 2) Guggenheim ^[2] presents a graph for different small molecules and 3) a 1980 thesis ^[3] has some data exemplifyig corresponding states for homogeneous nucleation.

For the Einstein viscosity law, the mathematics is such that all the polymer data fall on the same curve for $[\eta]$ M versus retention volume where $[\eta]$ is is the specific viscosity and M is the molecular weight polymer, so amazingly different polymers with differing molecular weights fall exactly on the same curve in Graph 1. The hydrodynamic volume does not matter because it has a 1-to-1 relationship with the retention volume.

Guggenheim has some data for small molecules for T/Tc vs $\rho/\rho c$ plotted and they all follow on the same curve as the reader can see in Graph 2.

In the 1980 thesis the small molecules fall on the same line for homogeneous nucleation data in Graph 3. Here are the two variables, first for the Y-axis then second for the X-axis for Eq. (3.17).

$$Y = (1 - Th/Tc) / m (J)$$
(4)

$$X = (1 - P/Pc)^{n} (J)$$
(5)

Sinha, the author of the thesis says, "If the quantum parameter Π is incorporated as a scaling unit in addition to the two Lennard-Jones parameters ε and σ in reducing the variables then a single curve should represent the behavior of both the classical and the quantum liquids." (Page 82 of)^[3].

Discussion 2

There is a corresponding states equation used for surface tension and the proof will be outlined here. It is from Guggenheim^[2]. First, Guggenheim has (6) from combining empirical formulae.

$$(\rho l - pg) / pc = (7/2) (1 - T/Tc)^{1/3}$$
 (6)

Then, from Katayama^[4], as Guggenheim cites.

$$\sigma y^{-2/3} = k (1 - T/Tc)$$
 (7)

Guggenheim says Katayama defines y in the following way.

$$y vc = (\rho l - pg) / pc$$
(8)

Where vc is a constant, the critical volume.

Combining (6) and (8) one gets.

$$y vc = (7/2) (1 - T/Tc)^{1/3}$$
 (9)

So

$$y^{-2/3} = (7/2 \text{ vc})^{-2/3} (1 - T/Tc)^{-2/9}$$
 (10)

Combining (7) and (10) gives.

$$\sigma = k (7/2 \text{ vc})^{2/3} (1 - T/Tc)^{11/9}$$
(11)

Which has to be rewritten as

$$\sigma = \sigma_0 (1 - T/Tc)^{11/9}$$
(12)

Where σ_0 is a constant for each liquid. The T/Tc means it is corresponding states. (12) Was used in Jennings^[5] to get the formula for bubble nucleation in polymer solutions.

Conclusion

In a review like this the author supposes it could easily be 30 pages long, but for those who read these words this is a taste of the concept of corresponding states. Physical Chemistry is mathematical and topical and was first unified by Josiah Willard Gibbs. Here are presented a few examples.

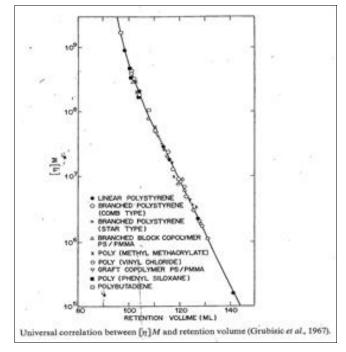
Acknowledgements

Deirdre Moy and Richard Swanberg have shown great

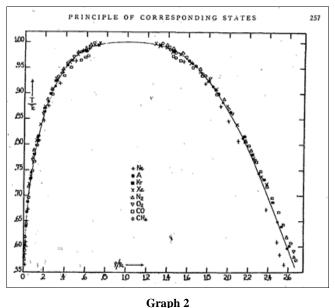
interest in my papers and encouraged me to write them. Deirdre is the mother of Kelly Moy, a friend since May 2010, and Rich is a high school classmate from ACALANES 1969, Lafayette, California who likes to read my papers.

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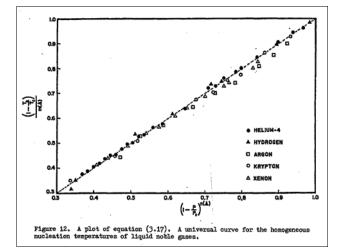
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Graph 3

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