

INTEGRATION OF THE CLAPEYRON EQUATION

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ABSTRACT

The Clapeyron differential equation has been integrated in closed form using a relative S -function, one resulting from a vantage point situation that exists between an observer and chemical phenomena being measured. A preliminary explanation for the need of relativity in chemistry is based upon the possible existence of weak quanta that move at slower speeds than photons and phonons.

INTRODUCTION

The S -function of an observed variable, v , measured on a linear scale in practice is defined as,

$$S(v) = \ln [(\ln v - \ln v_1)/(\ln v_2 - \ln v)] \quad (1)$$

where v_1 is the observer's apparent lower limit and v_2 is the corresponding upper limit for the finite domain of v . This means that the molecular domain from the observer's vantage point is changed from an apparent finite one to an infinite one by this transformation.

One problem involved in the use of definition (1) in a certain situation is establishing the observer's apparent domain limits. In the field of vapor-liquid equilibrium this is not difficult, since the liquid phase will not extend beyond the triple point or the critical region.

The rationale of this approach may be described as follows. Definition (1) is assumed as a postulate to compare transformed vapor pressure with transformed temperature for a few substances to rectify the data. This suggests the form of the integrated Clapeyron equation, and the differential equation is then obtained by the inverse operation. Several arguments are mentioned to suggest this is a unique result, and a tentative theory is proposed on the basis of the need for relativity in chemistry. Some areas for new work are also mentioned.

VAPOR PRESSURE

Classical thermodynamics predicts a functional relationship between vapor pressure and temperature in a vapor-liquid system at dynamic equilibrium, yet it does

not suggest the form of this relationship other than the differential Clapeyron restriction. The Clapeyron equation is somewhat unique in chemical science, having enjoyed a long lifetime since 1834. Therefore, we presume it as a postulate, since it involves observables, since it has been well checked with data, and since any derivation of it needs at least one postulate, so little simplification of logic occurs.

The Clapeyron equation involves five variables, and any four may be designated as independent with a fifth as the dependent variable: vapor pressure, temperature, latent heat of vaporization, liquid specific volume, and vapor specific volume. Since the last three are extensive variables, we presume there should be a relationship between the intensive variables on the one hand and the extensive ones on the other. We shall deal with the former in this paper. This distinction separates the variables, except it is usual to retain the vapor pressure with the extensive variables for the well-known form,

$$\frac{d \ln p}{d \ln T} = \frac{L_v}{p(V - V')} \quad (2)$$

where p is the vapor pressure, T is the temperature, L_v is the latent heat of vaporization, using the old terminology, and V and V' are the vapor and the liquid specific volumes, respectively.

We therefore seek a functional relationship that has four arbitrary constants with physical meaning and a fifth constant of integration. Any other mathematical form not meeting these parameter requirements must therefore be invalid. This essentially eliminates all of the functions in the literature except a few that happen to have five constants. However, in these remaining few, the constants have no physical meaning.

There are other restrictions and all of these are contained in the S -function, reasons why it was invented. The S -function allows dimensions to cancel in the transformation. This is also true of exponents and multiplying constants. Also, the inside logarithm operator is balanced, something not usually considered necessary.

However, some measurements often require an additive calibration that is not always easy to discover. This was the case in the early days of pressure measurement, and this was the case in establishing the Kelvin scale of temperature. A wrong additive factor will be retained in the S -function as a distortion.

Yet for the present work, the Kelvin scale appears to be satisfactory, and this situation is mentioned only in case a minor change is needed later. That is, if vapor pressure data for a certain substance were adopted as a standard, the right temperature additive could be compared with the present standard.

Since the essential purpose of this work is to provide a derivation of theory, only three examples have been selected: water, ammonia, and carbon dioxide. These compounds were selected because of data availability. No previous theory will rectify these three common substances with the same mathematics and allow a basis for comparison.

Since vapor pressure and temperature for the liquid phase have domain limits matching the triple point and the critical constants, these values are used in the S -transformation.

The suspected one-to-one correspondence, as noted by the 45° slope in Fig. 1, shows the value of this theory. Since the triple point and the critical values represent four arbitrary constants with physical meaning, the integration constant is the

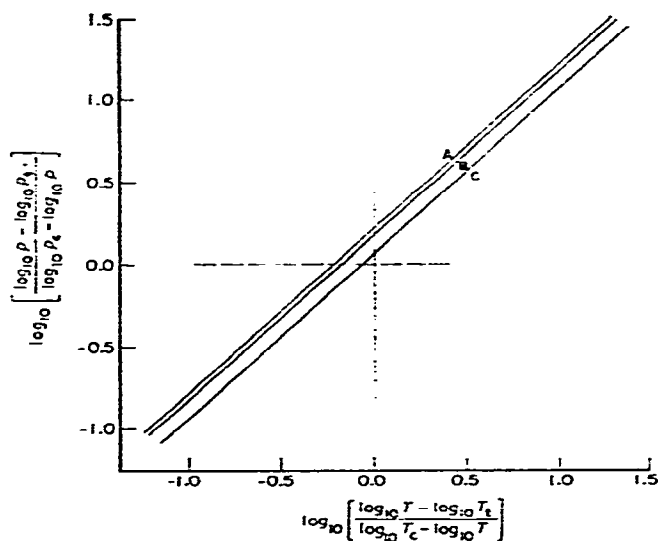


Fig. 1. S -plot of vapor pressure data for water (A), ammonia (B), and carbon dioxide (C) using data from Handbook of Chemistry and Lange's Handbook (calculations by Trescott Jensen, Kirk Nielson, and Patricia Larson, Department of Chemistry, Brigham Young University, July, 1970; drawing by Nora Del Murdock).

intercept for each substance in Fig. 1, if we arbitrarily designate temperature as the independent variable. The integrated Clapeyron equation is then rather simple in S -space,

$$S(p) = K + S(T) \quad (3)$$

The integration constant, K , is different for each substance and it should be finite, different from zero. Therefore it ought to match some aspect of molecular structure that now awaits discovery. This is a reason for this publication, since we feel something should result from this field.

CLAPEYRON EQUATION

Since the integration above has been performed by logic, it is necessary to show that the right differential equation can be obtained. Therefore, we differentiate

equation (3) to find,

$$\frac{d \ln p}{d \ln T} = \frac{\left(\ln \frac{p}{p_t} \right) \left(\ln \frac{p_c}{p} \right) \left(\ln \frac{T_c}{T_t} \right)}{\left(\ln \frac{T}{T_t} \right) \left(\ln \frac{T_c}{T} \right) \left(\ln \frac{p_c}{p_t} \right)} \quad (4)$$

Before testing (4), the following equation is found for one of the possible relationships involving the extensive variables, this time in terms of the intensive ones, since it is generally recognized that latent heat of vaporization may be expressed in terms of entropies, S and S' ,

$$\frac{S-S'}{V-V'} = \frac{p \left(\ln \frac{p}{p_t} \right) \left(\ln \frac{p_c}{p} \right) \left(\ln \frac{T_c}{T_t} \right)}{T \left(\ln \frac{T}{T_t} \right) \left(\ln \frac{T_c}{T} \right) \left(\ln \frac{p_c}{p_t} \right)} \quad (5)$$

In both (4) and (5) the t and the c subscripts refer to the triple point and the critical values.

To show (4) and (5) are valid, consider the region in which T approaches T_t , the triple point. The slope of p versus T in simple logarithmic space will be the discrete definition of this derivative, $\Delta \ln p / \Delta \ln T$. The same situation occurs in the critical region. It is sufficient to match one more point, and this will be considered theoretically at a later time. However, experimentally this is not difficult, since the latent heat of vaporization is often known at the normal boiling point. If specific volume data are not known, it is often possible to replace $p(V-V')$ with RT for technical purposes.

We feel this represents a satisfactory check on the theory, and a better check will be possible by plotting a number of compounds in S -space.

One note of caution appears necessary at this time. We feel that vapor pressure data may eventually become rather precise, so deviations from (3) and (4) should occur for the following reasons. No liquid can ever be purified completely. Molecules, especially polar ones, should have a tendency to dimerize or polymerize. If the K intercept for the polymerized form is different from that of the monomer, a systematic deviation should occur in regions where this occurs. Precise vapor pressure data therefore should be useful to note these situations to compare with other theory.

These complications are minimal, however, for the three substances in Fig. 1, else the data should deviate. Thus this method is a practical way to analyze mixtures. Some systems might not show a linear K dependence and therefore be interesting to analyze to advance the theory.

In systems where vapor pressure data are available only over a short range, the whole curve may be established by using various iteration methods combined with exact simultaneous solution of the equations obtained from five points, which is

reduced for each known domain limit. In the collection of vapor pressure data, the work may be distributed equally in S -space for a minimal effort.

If we prefer to solve for the vapor pressure to try to make the function look more like the conventional $\ln p$ versus $1/T$, the relationship will be, from (3),

$$\ln p = [\ln p_c \exp(K + S(T)) + \ln p_d / [1 + \exp(K + S(T))]] \quad (6)$$

WEAK QUANTA

We have the choice of regarding the above alleged integration as empirical or a valid solution in closed form. If the first viewpoint is adopted, this is the end of the story for the moment until new relationships are found and more systems analyzed. However, we feel there ought to be a better explanation of the logical development involving the vantage point situation existing between the observer and a measurement in chemistry.

Therefore, let it be supposed that the apparent observation of a domain is a relativity situation. If humans were blind, astronomy would be different. Molecules in a vapor-liquid system should behave about the same in the dark as in a weakly lighted situation. The same seems to be the case for moderate doses of phonons, although it is known that sound will disrupt the liquid order at higher intensity. Therefore, something else must be postulated to account for the relativity situation, why the observer cannot see the one-to-one correspondence between vapor pressure and temperature, even though his sensors and brain molecules are on the same level of order as the manifestations of the molecules in the system. After all, pressure and temperature are intensive properties.

Let us consider the domain of photons as far as a chemical observer is concerned. The light observable universe with the help of an electron microscope and a powerful telescope takes us from 10^{-3} cm to almost 10^{30} cm, a range ratio of about 10^{38} . The domain for phonons is less, since they cannot get off the Earth. Suppose we select the range ratio as 10^{13} , from 10^{-8} to perhaps 10^5 cm. This upper value may be designated as the dividing region between rarefied space and gases that have great mean free paths, above which the molecules may no longer be intact so that they are ionized and begin to behave like quantum waves in rarefied space. This gives us three particle states of matter (solid, liquid, and vapor states) and the domain for rarefied, outer space. Since phonons and photons also penetrate solids and liquids, this phase situation may be the key to the existence of weak quanta, moving at slower speeds than light and sound. That is, quanta responsible for taste transmission, using the convenient biochemical classification, should move through liquids and solids (polymers in biochemistry), while the quanta responsible for smell transmission should move only through solids. This choice is based upon the apparent body defense of moisture damping smell, while the taste defense is more a matter of dilution.

We do not know the exact laws that would suggest a simple relationship between these domains and speeds of these weak quanta, so let us assume some for the

sake of illustration. The taste quanta may be able to move through a domain of 10^{-8} to perhaps 10^{-4} cm with a maximum speed in the range of 100–500 cm/sec. The smell quanta may have speeds near 10–50 cm/sec and a much smaller domain, 10^{-8} – 10^{-6} cm.

To explain the relativity situation, it is only necessary to assume that the limiting velocities above may be approached in molecular interactions, so the observer sees a distorted view for a number of reasons: transmission, detection, and brain analysis of the molecular manifestations. The observer subjectively prefers a linear scale, since this is very convenient to him. However, he can use an *S*-function to put himself at the molecular interaction site without any distortion. If he can visualize a logarithmic domain, then all he needs is a linear relative transformation,

$$R(r) = \ln [(v - v_1)/(v_2 - v)] \quad (7)$$

However, definition (1) is more convenient for chemists than (7).

We have no way at this time to demonstrate the approach to relativity for the above postulated weak quanta, but we do have a good example for sound. The location of a jet plane by hearing versus sight is erroneous, as the plane approaches and exceeds the local sound velocity. Another possible example is the often presumed apparent expanding universe near 10^{30} cm, since we should not arbitrarily reject the idea of a larger domain where quanta move faster than light just because it does not suit classical theory. Something like this has also been suggested for the domain below 10^{-13} cm.

In short, we now have three particle states of matter and some logical arguments for a rarefied space, yet we have only two quanta, photons and phonons, to characterize the radiation that ought to occur between all matter to increase the disorder in the universe. Therefore, we may need two more types of weak quanta, at least in many fields of chemistry. Certainly we know that there is a large discrepancy between the latent heat of vaporization and pressure-volume change, as previously noted¹, and these additional molecular interactions should be indicative of the distortion caused by weak quanta. If each quantum is too weak, as we now suppose, to explain molecular interactions, it is possible that a number of these sum over a finite period of time. This is different from the unit quantum yield for photons in many areas of photochemistry. This would allow these weak quanta to occur without the kinetics being different from apparent first order mechanisms that seem to occur without cause.

CONCLUSION

The differential Clapeyron equation has been integrated using a relative *S*-function, a name selected because of its shape, whereas it was previously called a relative logarithmic transformation². Data may be plotted like the cases shown in Fig. 1, and the transformation may be as precise as the data collected, if a computer is used.

A new functional relationship for specific volumes and specific entropies for both phases at equilibrium is shown in (5). A direct solution of vapor pressure in terms of temperature is shown in (6), and this may be compared with conventional methods, if desired.

We think the reason the simple one-to-one correspondence occurs in S -space but cannot be noted by the observer is a result of the existence of weak quanta producing relativity distortions in the chain of transmission between the molecules in a liquid system as well as the subjective linear scale used by the observer.

Different compounds should be comparable in S -space to note the dependence on molecular structure, as indicated by the K value in (3) and in (7).

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