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RECASTING THE DERIVATION OF THE CLAPEYRON EQUATION INTO A CONCEPTUALLY SIMPLER FORM

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Abstract. The Clapeyron equation specifies the variation of the pressure, P, with respect to the temperature, T, of a closed two-phase one component system at the phase boundary under conditions of thermodynamic equilibrium. Even though in the context of the traditional derivation of this equation (as presented in most books on undergraduate/postgraduate Physical Chemistry or Thermodynamics), $G_{m,i}(P, T)$ (where i = 1 and 2) curves are not presented, the derivation involves the consideration of two points on each of these curves subject to the condition that the two phases are in equilibrium with each other. Geometrically, this implies the separate movement from an initial to a final point (in the neighborhood of the initial point) on the two $G_{m,i}(P, T)$ (where i = 1 and 2) curves which incidentally are congruent at the phase boundary. At first glance, however, it is not trivial to geometrically (graphically) visualize this movement from the equations that are presented in the tradiational derivation of the Clapeyron equation, thereby, possibly causing a certain amount of confusion. In the present work, a conceptually simpler and mathematically rigorous derivation of the Clapeyron Equation is presented where the quantity of interest that is considered is $\Delta G_m(P,T) = G_{m,1}(P,T) - G_{m,2}(P,T)$. $\Delta G_m(P,T)$ is equal to zero at the phase boundary and, thereby, $d\Delta G_m(P,T)$ is also equal to zero at the phase boundary. This key idea then makes it possible to focus on a single point in the $\Delta G_m(P, T)$ curve that occurs at the phase boundary between the two phases in deriving the Clapeyron Equation and also to geometrically visualize the phase equilibrium situation.

Keywords: Clapeyron equation, phase equilibria, chemical thermodynamics, molar Gibbs energy, equilibrium thermodynamics

The Clapeyron equation

The Clapeyron equation (Atkins & Paula, 2003) shown in Eq. (1) determines the variation in the pressure, P, with respect to the temperature, T, of a closed one component system that contains two phases, 1 and 2, which are in equilibrium with each other.

$$\frac{dP}{dT} = \frac{\Delta S_m}{\Delta V_m} \tag{1}$$

In Eq. (1), it is important to note that ΔS_m represents the difference in molar entropies of the two phases namely, phase 1 and phase 2, while ΔV_m represents the difference in molar volumes of these two phases.

Relevant thermodynamic quantities

We now consider thermodynamic quantities that are of relevance in the derivation of the Clapeyron equation (1) as shown above. G_m is the molar Gibbs energy of the substance in a certain phase which is also equal to the chemical potential μ of that substance in that phase. In a closed one component system both G_m and μ can be expressed as shown by Eqs. (2) and (3), respectively.

$$G_m = G_m\ (P,T) \tag{2}$$

$$\mu = \mu\ (P,T) \tag{3}$$

Since the equivalence of both G_m and μ has been pointed out above, it suffices that we can work with either quantity in the following text, and we shall choose to use G_m. From Eq. (2), employing the method of calculus (Barrante, 2004), we get Eq. (4).

$$dG_m = \left(\frac{\partial G_m}{\partial T}\right)_P dT + \left(\frac{\partial G_m}{\partial P}\right)_T dP \tag{4}$$

From any of the physical chemistry texts, e.g. (Atkins & Paula, 2003; Castellan, 1996; Engel & Reid, 2007), it can be ascertained that Eqs. (5) and (6) hold. Here S_m and V_m are respectively the molar entropy and the molar volume of the system under consideration.

$$\left(\frac{\partial G_m}{\partial T}\right)_p = -S_m \tag{5}$$

$$\left(\frac{\partial G_m}{\partial P}\right)_T = V_m \tag{6}$$

Key steps in the traditional derivation of the Clapeyron equation

The derivation of the Clapeyron equation can be found in many physical chemistry or thermodynamics texts (Atkins & Paula, 2003; Castellan, 1996; Engel & Reid, 2007; Blundell & Blundell, 2008; Kaufman, 2002).

The central tenet in these derivations is the recognition of the fact that at equilibrium Eq. (7) holds.

$$G_{m,1} = G_{m,2} \tag{7}$$

In this equation $G_{m,i}$ (for $i = 1$ and 2) represents the phase boundary between phases 1 and 2 at each point along the phase boundary. Therefore, it is customary in the derivation of the Clapeyron equation (1) to consider Eq. (8).

$$G_{m,1} + dG_{m,1} = G_{m,2} + dG_{m,2} \tag{8}$$

It must be noted that in Eq. (8) it is presupposed that $(G_{m1,} G_{m,2})$ represents one particular point, a, in the phase boundary between phases 1 and 2, while $(G_{m1} + dG_{m1}, G_{m,2} + d G_{m2})$ represents another point, b, in the phase boundary of these two phases. However, point b is in the neighborhood of point a. Nonetheless, the left hand side describes the variation of the molar Gibbs energy on one curve while the right hand side describes the variation of the molar Gibbs energy on another curve. *Incidentally, the two curves are congruent at the phase boundary for a closed one component system.* However, the two curves are typically described by different equations. When $G_{m,i}(P, T)$ (for $i =$ 1 and 2) curves are plotted against the variables P and T,we find that any point on the line of intersection of these two curves which occurs at the phase boundary represents a cross-over.

To the best of my knowledge, I have not seen the above facts explicitly stated in any of the relevant texts alluded to above. In these texts, Eq. (7) and (8) are used in a mathematical sense but the curves representing the molar Gibbs energy curves are ignored. Not being able to visualize this is a handicap of the derivations that are presented. In this paper, therefore, I have made an attempt to capture the variation of the difference in the molar Gibbs energies of the two phases in question in the derivation of the Clapeyron equation and to provide a graphical representation of the situation under which the Clapeyron equation is derived.

It must be noted that from Eq. (7) and (8) we get Eq. (9) that then leads on to the Clapeyron equation (which will be derived fully in the next section using the new approach).

$$dG_{m,2} = dG_{m,2} \tag{9}$$

New approach to the derivation of the Clapeyron equation

As has already been expressed in Eq. (7), we know that for two phases of a closed one component system to be in equilibrium, the molar Gibbs energy of the two phases must be equal. Therefore, proceeding from Eq. (7) we get Eq. (10).

$$\Delta G_m = G_{m,1} - G_{m,2} = 0 \tag{10}$$

We now focus attention on ΔG_m and note that it is a constant which is equal to 0 in this particular case. Eq. (11) follows from Eq. (10) because the differential of a constant is zero. This can be verified by studying a suitable mathematics text (Barrante, 2004).

$$d\Delta G_m = 0 \tag{11}$$

Fig. 1 is a plot of the variation of ΔG_m with respect to P and T subject to the constraints imposed by Eqs. (10) and (11). What this approach does is that it enables us to recognize both algebraically and geometrically that the quantities of interest are ΔG_m and $d\Delta G_m$ which act as physical constraints that determine the phase boundary between phases 1 and 2.

There are three key points to note at this stage: (1) The new approach makes it possible to comprehend both algebraically and geometrically the functional dependence of the phase boundary on the molar Gibbs energies of the two phases; (2) In this derivation we focus upon a single point in the phase boundary as represented by Fig. 1 without resorting to a mathematical excursion on what is the congruent region of two different curves- a point that may elude certain readers at least at a first reading of the topic, and (3) Since the co-existence curve of the two phases 1 and 2 lies entirely on the PT plane, P and T are constrained to vary in such a way so as to ensure the validity of Eq. (11).

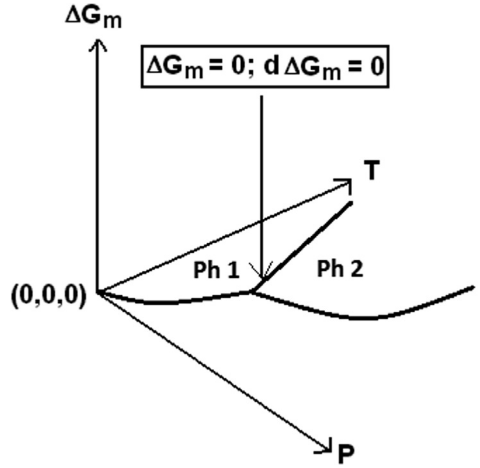

Fig. 1. A diagrammatic representation of the locus of points on the ΔG_m *(P, T)* surface that corresponds to ΔG_m *(P, T) = 0* and by extension to $d\Delta G_m$ *(P, T) = 0*. Ph 1 and Ph 2 represent the regions where phase 1 and phase 2, respectively, are the stable phases under conditions of equilibrium thermodynamics

By making use of Eqs. (4), (5), (6) and (11), we get Eq. (12) where $S_{m,i}$ and $V_{m,i}$ represent the molar entropies and the molar volumes of the i^{th} phase where $i = 1$ and 2.

$$-(S_{m,1} - S_{m,2})\, dT + (V_{m,1} - V_{m,2})\, dP = 0 \tag{12}$$

Rearrangement of Eq. (12) yields Eq. (1) which is the Clapeyron equation.

$$\frac{dP}{dT} = \frac{\Delta S_m}{\Delta V_m} \tag{1}$$

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