

Lambda versus firstorder transitions

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to deliver the course. The 1 semester-hour course described here required an average of about 5 instructor hours per week, the time being greater at the beginning and tapering off to the end. This figure would presumably be reduced as students and instructor both became more accustomed to the new mode.

XIV. THE NEED FOR GRAPHICS

All participants in the course felt hampered by the missing chalkboard. The use of prepared illustrations for discussion addressed this problem to a small degree, but a general solution to this problem must be found before the conference mode can be widely adapted to physics courses. The use of computer graphics to support a text-based discussion is an obvious response, but conventional graphics in this application suffer from two major drawbacks: (1) The information in a graphics screen requires several minutes for transmission over a telephone line, depending on the complexity and size of the picture; and (2) graphics information is critically dependent on terminal hardware. Instructions to paint a graphics image on an Apple screen, say, mean nothing to an IBM machine. It is unreasonable to insist that all conference participants, perhaps scattered over wide distances, have identical computers.

A promising approach to this problem is that offered by the North American Presentation Level Protocol Syntax (NAPLPS),¹¹ a software standard for transmitting drawing instructions rather than the graphic itself. NAPLPS includes such primitives as circle, arc, and fill, and additionally can change entire screen attributes (colors, text fonts, etc.) with the transmission of a single byte. Instructions for recreating a quite complicated graphic can be transmitted via modem in only a few seconds.

Each conference participant seeking to use NAPLPS graphics must have appropriate encoding and decoding software, but at least the compatibility issue of point 2 above is converted from a hardware to a software problem.

XV. CONCLUSIONS

Computer conferencing offers the promise of delivering physics courses at a distance, and taps and develops verbal skill within students that is largely undeveloped in traditional lecture courses. The two principal drawbacks to using this mode for physics courses are (1) the lack of suitable telecommunications graphics, and (2) the severe drain on instructor time to conduct the conference. We continue work at The University of West Florida in seeking solutions to these problems.

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Lambda versus first-order transitions

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If the lambda transition of, say, helium is regarded as taking place over a temperature region, then an integrated latent heat and latent volume that satisfy a Clausius-Clapeyron equation can be defined. The situation is analogous to what happens in ordinary first-order transitions, which suggests a generalization of the Ehrenfest classification scheme for transitions.

I. INTRODUCTION

In the lambda transition of, say, liquid helium, entropy and volume are continuous at the transition temperature T_λ , but the heat capacity C_P and expansivity β_P show peaks there. Integration over the peaks at constant pressure

P allows the definition of latent heats and volumes spread over a few degrees of temperature. The ratio of these is just the slope of the transition curve at P , i.e., the Clausius-Clapeyron equation holds in this integrated sense. These results imply that the Ehrenfest classification scheme for transitions can be generalized.

In Sec. II, we describe a proof of the Clausius–Clapeyron equation for first-order transitions that will prove useful when we come to lambda transitions. Some background on these is provided in Sec. III, while the arguments for the latent heats, etc., in them is contained in Sec. IV. Transition schemes are discussed in Sec. V.

The derivations of the Clausius–Clapeyron equation in Secs. II and IV are rather unusual. We thought it of interest to survey the amazing number of proofs that can be made of this equation, and those are contained in the Appendix.

II. THE CLAUSIUS–CLAPEYRON EQUATION AS A MAXWELL RELATION FOR G

About a half century after Gibbs (1876) emphasized the importance of the Gibbs free-energy G in analyzing phase transitions,¹ Ehrenfest² suggested a classification scheme based on the lowest derivative of G that exhibits discontinuities at the transition temperature.³ A “first-order” transition displays discontinuities in the first derivatives of G , i.e., in the entropy S ($= -\partial_T G$) and volume V ($= \partial_P G$). Our notation assumes that $G = G(P, T)$ so that $\partial_T G = (\partial G / \partial T)_P$, etc. In first-order transitions, the Clausius–Clapeyron equation connects the discontinuities ΔS and ΔV of entropy and volume with the slope dP_z/dT of the transition curve denoted $P_z(T)$ or $T_z(P)$ at that point:

$$\frac{\Delta S}{\Delta V} = \left(\frac{dP}{dT} \right)_z. \quad (1)$$

A “second-order” transition has discontinuities in the second derivatives of G such as the heat capacity C_P at constant pressure and the expansivity β_P ,

$$C_P = T \partial_T \partial_T G = -T \partial_T S, \quad (2)$$

$$\beta_P = V^{-1} \partial_T \partial_P G = V^{-1} \partial_T V, \quad (3)$$

but not in the first derivatives. In this case, Eq. (1) obviously has no relevance since S and V are continuous; instead the “Ehrenfest relation”

$$\frac{\Delta C_P}{TV \Delta \beta_P} = \left(\frac{dP}{dT} \right)_z \quad (4)$$

holds. (This was actually first derived by W. H. Keesom.) There is another Ehrenfest relation for second-order transitions and third-order transitions are defined in an analogous way.

It should be pointed out that Eq. (4) can be derived from Eq. (1) if we use L’Hopital’s rule and expand ΔS and ΔV in powers of $T - T_z(P) = dT$ along the isobar on both sides of the transition curve, i.e., if we write

$$\begin{aligned} \Delta S &= S(T_z + dT, P) - S(T_z - dT, P) \\ &= (\Delta S)_z + (\partial_T S)_{T_z+0} dT - (\partial_T S)_{T_z-0} dT + \dots \\ &= (\Delta C_P)_z dT + \dots \end{aligned} \quad (5)$$

The ratio $\Delta S/\Delta V$ then gives $\Delta C_P/TV \Delta \beta_P$ in the limit $dT \rightarrow 0$.

We now wish to show that Eq. (1) can be derived as a Maxwell relation for G . We assume that a transition line $T_z(P)$ exists in PT space, that on the low-temperature side lies phase 2 with Gibbs function $G_2(P, T)$, and that on the high-temperature side lies phase 1 with Gibbs function $G_1(P, T)$ so that at any P, T ,

$$G(P, T) = [1 - \theta(t)]G_2(P, T) + \theta(t)G_1(P, T). \quad (6)$$

Here,

$$t = T - T_z(P) \quad (7)$$

and $\theta(t)$ is the step function

$$\begin{aligned} \theta(t) &= 1 \cdots t > 0 \\ &= 0 \cdots t < 0. \end{aligned} \quad (8)$$

If t is positive, then $T > T_z$ and point P, T is in phase 1; if t is negative, then the point is in phase 2 (where $1 - \theta$ has the value 1).

The Gibbs energy is continuous at the transition line:

$$G_1(P, T_z(P)) = G_2(P, T_z(P)). \quad (9)$$

Further, the derivative of the step function, $d\theta/dt$, is the delta function $\delta(t)$, whence

$$\partial_T \theta(t) = \delta(t), \quad (10a)$$

$$\partial_P \theta(t) = -\frac{dT_z}{dP} \delta(t), \quad (10b)$$

$$t \delta(t) = 0. \quad (10c)$$

We are now in a position to make the proof. From Eq. (6), the first derivatives of G are

$$\partial_T G = -S = -(1 - \theta)S_2 - \theta S_1, \quad (11a)$$

$$\partial_P G = V = (1 - \theta)V_2 + \theta V_1, \quad (11b)$$

where $S_1 = -\partial_T G_1$, and so on. One might expect that a delta function $\delta(t)$ would occur in these equations, by the definition in Eq. (10a), but all such terms would appear in the combination $(G_1 - G_2)\delta(t)$, which by Eq. (10c) is zero.

The end of the proof comes about by computing the second derivatives of G or, in other words, the first derivatives of Eqs. (11):

$$\begin{aligned} \partial_T \partial_T G &= [1 - \theta](-\partial_T S_2) + \theta(-\partial_T S_1) \\ &\quad - \delta(t)T(S_1 - S_2), \end{aligned} \quad (12a)$$

$$\begin{aligned} \partial_P \partial_T G &= [1 - \theta](-\partial_P S_2) + \theta(-\partial_P S_1) \\ &\quad - \delta(t) \frac{-dT_z}{dP} (S_1 - S_2), \end{aligned} \quad (12b)$$

$$\partial_T \partial_P G = [1 - \theta] \partial_T V_2 + \theta \partial_T V_1 + \delta(t)(V_1 - V_2), \quad (12c)$$

$$\begin{aligned} \partial_P \partial_P G &= [1 - \theta] \partial_P V_2 + \theta \partial_P V_1 \\ &\quad + \delta(t) \frac{-dT_z}{dP} (V_1 - V_2). \end{aligned} \quad (12d)$$

Consider first-order transitions. Then latent heats and volumes exist, hence $S_1 - S_2 \neq 0$, and $V_1 - V_2 \neq 0$, and the delta function terms in Eqs. (12) do not drop out. The Maxwell relation for G now consists of the statement

$$\partial_P \partial_T G = \partial_T \partial_P G, \quad (13a)$$

$$\text{Eq. (12b)} = \text{Eq. (12c)}, \quad (13b)$$

which is simply the condition that P and T are independent variables in G .

In implementing Eq. (13b), we see that the terms proportional to $1 - \theta$ must satisfy it by themselves, since there can be no compensation from the terms in θ or δ . Similarly, the θ terms must satisfy Eqs. (13) by themselves. These all give the usual Maxwell relations for G . But the terms proportional to $\delta(t)$ must also satisfy Eq. (13), and these give the Clausius–Clapeyron equation, by inspection. [Com-

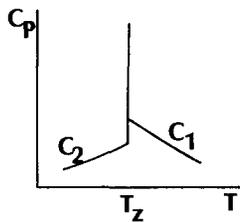


Fig. 1. A diagram of the heat capacity C_p of a substance that undergoes a first-order transition. The latent heat and volume are contained in the delta function peak.

pare with Eq. (1).] Thus the Clausius–Clapeyron equation may be regarded as part of the Maxwell relations for G .

If we wish to consider second-order transitions, then the delta function terms in Eqs. (12) drop out, since S and V are now continuous at the transition. Third derivatives on G will produce new nonzero delta function terms, which, in the following *generalized Maxwell relations*,

$$\partial_p \partial_T \partial_T G = \partial_T \partial_T \partial_p G, \quad (14a)$$

$$\partial_p \partial_T \partial_p G = \partial_T \partial_p \partial_p G, \quad (14b)$$

yield the Ehrenfest relations. Equation (14a) gives Eq. (4).

One final remark: Eq. (12a), if multiplied by $-T$, gives the heat capacity C_p ,

$$C_p = [1 - \theta] C_{p,2} + \theta C_{p,1} + L \delta(t) \cdots T = T(S_1 - S_2), \quad (15)$$

where L is the latent heat. This expression has the virtue of containing the heat capacities in the two phases and the latent heat all together. It is depicted schematically in Fig. 1. Notice that there is a delta function singularity at T_z , which says, of course, that at T_z a flow of heat does not produce a change in temperature.

There are easier ways of proving the Clausius–Clapeyron equation than this.³ We have used the Maxwell relation approach here because it suggests a link to the lambda transitions to be discussed in the following sections.

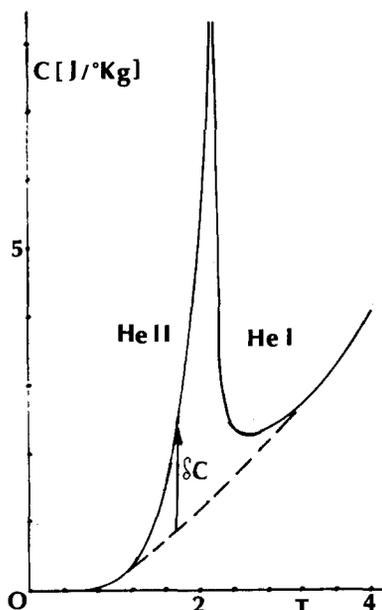


Fig. 2. The heat capacity at saturated vapor pressure for liquid helium near the HeI–HeII transition. The solid line represents the observed values. The dashed line is a conjectured “normal” heat capacity, joining smoothly the high- and low-temperature segments. The deviation δC from the normal is the anomalous heat capacity that can be correlated with a Clausius–Clapeyron equation. The data were taken from Table A1 of Ref. 10.

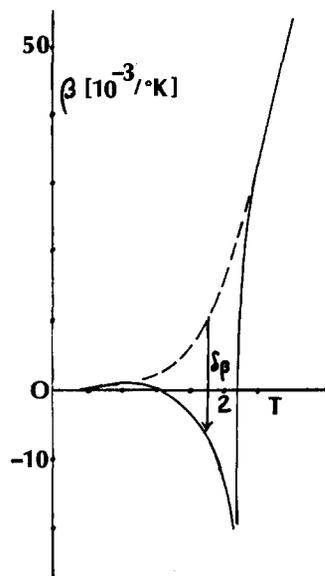


Fig. 3. The expansivity for liquid helium near the HeI–HeII transition. The solid line represents the observed values, the dashed line the conjectured “normal” expansivity. The deviation $\delta\beta$ from the normal is the anomalous expansivity that can be correlated with the Clausius–Clapeyron equation. The data were from Table A1 of Ref. 10.

III. LAMBDA TRANSITIONS

In the 19th century, the theory of phase transitions was involved with explaining, in large part, boiling and melting, with their latent heats and volumes and Clausius–Clapeyron equation at the transition temperature T_z . In the 1920s, however, Keesom⁴ and coworkers discovered that liquid helium experiences what has to be a transition at about $T = 2.19 \text{ K} = T_\lambda$, but there is no latent heat or volume. What appear are peaks in the heat capacity C_p and expansivity β_p as shown⁵ in Figs. 2 and 3. The λ shape of C_p gave rise to the name lambda transition. Initially, it was thought that C_p and β_p undergo discontinuities at T_λ , which prompted Keesom to find an analogue to the Clausius–Clapeyron equation,⁶ namely, Eq. (4) above, and Ehrenfest to develop his scheme for classifying phase transitions (see Secs. II and V).

Lambda transitions occur in a number of guises, but they all demonstrate the feature that a structural change starts to occur at T_λ and is completed at $T = 0$. In helium, the change is from a normal to a super fluid at $T = 0$. In beta-brass (CuZn), the change is from a disordered state to an ordered one at $T = 0$. In some magnetic materials, the change is from a paramagnetic configuration to an antiferromagnetic one at $T = 0$. This is in contrast to first-order transitions, where the structural change takes place all at once at T_z , where the substance is a mixture of two phases separated in space.

Nevertheless, it is also possible to imagine a “two-fluid” situation between T_λ and $T = 0$ in λ transitions [e.g., partly normal, partly superfluid in helium (Tisza, Landau); partly ordered, partly disordered in beta-brass, etc.] But there is no separation in space of these fluids; a given atom is not entirely in one phase or the other. In a statistical sense, there are two types of global excitations. At T_λ , the system is purely of one type; at $T = 0$, it is purely of the other.

This pattern was picked up by Landau⁷ in 1937, although the superfluid property in helium had not yet been established, and he argued that the significant thing that happened at T_λ was a change in *symmetry* announcing, so to speak, the beginning of a gradual change in structure. To

describe the change, Landau introduced an order parameter η designed to go from 0 at T_λ to 1 at $T = 0$, charting the progress from one fluid to the other, and he expanded the Gibbs function G in powers of η near T_λ :

$$G(P, T, \eta) = G_0 + \eta^2 G_2 + \eta^3 G_3 + \dots \quad (16)$$

Here, G_0, G_2 , etc., are some functions of T and P , while η was determined by minimizing G . The functions η and G_2 were found by his procedure to be functions of the t of Eq. (7),

$$t = T - T_\lambda(P). \quad (17)$$

By this formalism, Landau was able to produce continuous G, S , and V , discontinuous C_p and β_p , and to follow the system away from T_λ . We shall not attempt to fill in any of the details.

In the 1950s, it became apparent by theoretical conjecture (Tisza) and experimental verification that C_p and β_p do not suffer ordinary discontinuities at T_λ , but seem to diverge logarithmically there, implying that the λ transitions do not fit into the Ehrenfest classification scheme. Pippard⁸ in 1957 and Buckingham and Fairbank⁹ a few years later analyzed what happens near the singularity and developed equations (the PBF equations) that should be valid asymptotically as $t \rightarrow 0$. The one of interest here is

$$\frac{C_p}{TV\beta_p} = \frac{dP_\lambda}{dT} \quad (t \rightarrow 0), \quad (18)$$

where the function $P_\lambda(T)$ denotes the line of λ transitions in PT space. This equation reminds us of Eq. (4). In fact, if there were a discontinuity, one could take the difference of Eq. (18) across the transition and obtain Eq. (4), as Buckingham and Fairbank showed. We shall not derive Eq. (18) in the original way but a derivation of another type will be given in Sec. IV.

IV. LAMBDA TRANSITIONS REVISITED

In a certain sense, the Clausius–Clapeyron equations survive even in the λ transition of liquid helium. To see this, we notice that in comparing Fig. 2 with Fig. 1, the λ transition does not exhibit a delta function singularity in C but does exhibit a peak, and similarly with β . This suggests that if we integrate C and β over the range of the peaks (subtracting off the “normal” C and β), we can define a quasi-latent entropy δS and volume δV by

$$\frac{\delta S}{M} = \int T^{-1} \delta c \, dT, \quad (19)$$

$$\frac{\delta V}{M} = \int \rho^{-1} \delta \beta \, dT, \quad (20)$$

where M is the mass of the specimen, c is the heat capacity per mass, and ρ is the mass density. The quantities δc and $\delta \beta$ are the differences of the true values from hypothetical “normal” values obtained by the free-hand extrapolations shown as the dashed lines in Figs. 2 and 3. These dashed lines are to some extent arbitrary, but it is significant that the numbers obtained for δS and δV give a ratio $\delta S/\delta V$ that equals approximately $(dP/dT)_\lambda$, i.e., that satisfies the Clausius–Clapeyron equation. (We used $C_{\text{sat vap press}} \cong C_p$ implicitly.)

The crudeness of the graphical approach just described cries out for a more analytic argument. This can be made as follows. Suppose that the Gibbs free-energy G is composed

of a normal term $G_0(P, T)$ and an anomalous term $G_\lambda(t)$. The latter is associated in some way with the transition temperature, and we assume that it depends primarily on the variable t of Eq. (17) that was used extensively by Landau and by Buckingham and Fairbank, as described in Sec. III. Thus

$$G = G_0(P, T) + G_\lambda(t). \quad (21)$$

A separation of this type is quite close to what Landau used in Eq. (16) above, and to a form inferred by Buckingham and Fairbank.⁹ It is understood that for temperatures sufficiently below T_λ , G must approach zero to satisfy the Third Law.

The plan is now to proceed just as we did in Sec. II, starting from Eq. (6). There the t -dependent factor was the step function $\theta(t)$, which eventually led to a delta function singularity. Here, we have not specified what the t dependence is, and we shall not need to know it, but, if we wish to be led to a logarithmic singularity, we could choose

$$G_\lambda(t) = At^2 \ln|t| + Bt^2 \theta(t), \quad (22)$$

where A and B are constants. The first term is the limiting form of the known solution to a two-dimensional problem,¹¹ but here it is just a useful function near T_λ .

Following the argument of Sec. II, we take derivatives of G to find

$$S = S_0 + S_\lambda = -\partial_T G_0 - \frac{dG_\lambda}{dt}, \quad (23)$$

$$V = V_0 + V_\lambda = \partial_P G_0 - \frac{dG_\lambda}{dt} \frac{dT_\lambda}{dP}, \quad (24)$$

$$C_p = C_{p,0} + C_{p,\lambda} = T \partial_T S_0 + T \Delta S_\lambda \Lambda(t), \quad (25)$$

where

$$\Lambda(t) = \frac{dS_\lambda/dt}{\Delta S_\lambda}. \quad (26)$$

Here, ΔS_λ is a normalizing factor that we take to be the total change in S_λ across the transition.

The $\Lambda(t)$ has the units of $1/t$ and plays the role in λ transitions that $\delta(t)$ does in first-order transitions. [Compare the last terms of Eqs. (25) and (15).] It is a peaked function resembling Fig. 2 and spread out over several degrees. Further, ΔS_λ plays the role here that $S_1 - S_2$ played there. The last terms in Eqs. (25) and (15) differ primarily in that the anomalous peaking occurs right at $t = 0$ in first-order transitions, but is spread out over a few degrees here.

To get the Clausius–Clapeyron equation in Sec. II, we took further derivatives on S and V [see Eqs. (12)]. We cannot proceed that way here, since the latent heats and volumes do not occur at one given temperature. We can, however, take differences δS_λ and δV_λ , at constant pressure, of the anomalous terms, between two temperatures apart a finite amount. From Eqs. (23) and (24), we get

$$\delta S_\lambda = \delta \frac{-dG_\lambda}{dt}, \quad (27)$$

$$\delta V_\lambda = -\frac{dT_\lambda}{dP} \delta \frac{-dG_\lambda}{dt}. \quad (28)$$

In taking δV_λ , we used the fact that dT_λ/dP is defined at the transition line and does not change along an isobar. It comes out from under the δ operation. The ratio gives

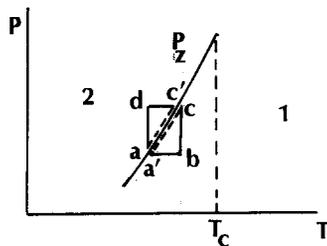


Fig. 5. A liquid-vapor phase diagram of PT space. A point on the transition curve corresponds to a horizontal line in the "dome" of Fig. 4. The points a, a', \dots here are not the same as in Fig. 4.

was applied to the loop $aa'b'ba$ of Fig. 4, although he did not use such diagrams (1 kg of water is boiled at 100°C and P_A , cooled to and condensed at 99°C and P_B , reheated to 100°C and P_A , and so on). The work done is $dW = \delta P \Delta V$, where $\delta P = P_A - P_B$ and $\Delta V = V_{a'} - V_a$. Carnot estimated ΔV as the vapor volume only. Heat Q_A enters during aa' , Q_B leaves during bb' , and steps $a'b'$ and ab are neglected. On the caloric theory, $Q_A = Q_B = Q$. Thus

$$\delta P \Delta V / Q = dF(T). \quad (\text{A1})$$

Not knowing $F(T)$, the most Carnot could do in verifying his theory was to show that it is the same for the water-steam cycle as for an air cycle.

(3) Clapeyron¹⁸ used the cycle $cc'd'dc$ of alternating isotherms and adiabats of Fig. 4, wrote $dF = dT/C(T)$, where C is now unknown, and clearly labeled ΔV as the difference in volume in the two phases. Thus Eq. (A1) became

$$\frac{\Delta V}{Q} = C^{-1} \frac{dT}{dP}. \quad (\text{A2})$$

Here, dT and dP are the differences between the lines cc' and dd' of Fig. 4. But line cc' corresponds to a point on the transition curve on Fig. 5, and line dd' corresponds to a neighboring point on that curve. Thus dP/dT is the slope of the transition curve, i.e., $dP_z(T)/dT$. This identification will be needed in many of the proofs. We might call Eq. (A2) Clapeyron's equation.

(4) Clausius¹⁹ in 1850 abandoned the caloric theory, and had to distinguish the input heat Q_A during cc' of Fig. 4 from the output heat Q_B during dd' . He was able to preserve Carnot's maximum efficiency expression in the form $dW/Q_B = dT/C$, using Clapeyron's C . He also argued that, for an infinitesimal cycle, $Q_B \cong Q_A$ even on the mechanical theory, whence Eq. (A2) is found again. In addition, from Kelvin's work, he identified C as T (for a discussion, see the next paragraph), and the equation has arrived at its final form,

$$\frac{\Delta V}{Q} = T^{-1} \frac{dT}{dP}. \quad (\text{A3})$$

(5) In 1854, Kelvin²⁰ analyzed the thermoelectric problem by writing the first and second laws of thermodynamics as $\oint dU = 0$ and $\oint dQ_{\text{rev}}/T = 0$ (where "rev means "reversible"). He did not apply these to the phase transition cycle $cc'd'dc$ of alternating isotherms and adiabats in Fig. 4, but, if we do, we get,

$$\oint dU = Q_A - Q_B - W = 0, \quad (\text{A4})$$

$$\oint \frac{dQ_{\text{rev}}}{T} = \frac{Q_A}{T_A} - \frac{Q_B}{T_B} = 0, \quad (\text{A5})$$

where W is the work done by the system in the cycle. Now, use Clapeyron's $\delta P \Delta V$ for W , substitute Q_B from Eq. (A5) into (A4), and let $T_A - T_B = dT$. We regain Eq. (A3).

The maximum efficiency expression used by Carnot and Clausius is contained in Eq. (A5). In fact, if Eqs. (A4) and (A5) are decoupled, we find $W/Q_A = 1 - T_B/T_A$, which is the *general* expression for maximum efficiency. For an infinitesimal cycle, this reduces to $W/Q = dT/T$, whence Clapeyron's C is T , and Carnot's F is $\ln T$. If we write $dQ_{\text{rev}}/T = dS$, where S is entropy, then Eq. (A5) is conservation of entropy.

(6) Gibbs²¹ generalized the equation to heterogeneous systems in 1875. In the one-component limit, his argument is seen to rest on the Gibbs-Duhem relation,

$$d\mu = (S/N)dT - (V/N)dP, \quad (\text{A6})$$

which relates situations in which the intensive variables μ , T , and P differ only slightly. Here μ is the chemical potential and N is the number of particles in the system. Gibbs applied Eq. (A6) to the liquid portions ("L") at states m and n of Fig. 4,

$$d\mu_L = (S/N)_L dT - (V/N)_L dP \quad (\text{A7})$$

and to the vapor portions ("v") at m and n ,

$$d\mu_v = (S/N)_v dT - (V/N)_v dP, \quad (\text{A8})$$

and equated them, since $\mu_L = \mu_v$ in equilibrium. Alternatively, one could just take $\oint d\mu = 0$ around the cycle $aa'b'cc'da$ of Fig. 5. In either case, one gets

$$\frac{\Delta S}{\Delta V} = \frac{dP}{dT}, \quad (\text{A9})$$

which is the Clausius-Clapeyron equation, since $Q = T \Delta S$.

Notice that the integral $\oint dZ$ around a loop in state space of *any* state variable Z is zero. This feature is used frequently, as, for example, in Eqs. (A4) and (A5).

(7) The Helmholtz free-energy $F = U - TS$ satisfies $dF = -S dT - P dV$ if we ignore changes in particle numbers. A Maxwell equation is

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V. \quad (\text{A10})$$

Applied to state m of Fig. 4, this is immediately the Clausius-Clapeyron equation. It corresponds to the equation $\oint dF = 0$ taken around the loop $mnn'm'm$ in Fig. 4.

(8) The enthalpy $H = U + PV$ satisfies $dH = T dS + V dP$. A Maxwell equation is

$$\left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S. \quad (\text{A11})$$

Applied to point d of Fig. 4, this is immediately the Clausius-Clapeyron equation. It corresponds to the equation $\oint dH = 0$ around the loop $dcc'd'dc$ of Fig. 4.

(9) Finally, Buckingham and Fairbank⁹ gave an interesting derivation by integrating

$$\begin{aligned} dS &= \left(\frac{\partial S}{\partial P}\right)_T dP + \left(\frac{\partial S}{\partial T}\right)_P dT \\ &= -\left(\frac{\partial V}{\partial T}\right)_P dP + \left(\frac{\partial S}{\partial T}\right)_P dT, \end{aligned} \quad (\text{A12})$$

where the second form used the Maxwell relation from $dG(P,T)$. Let the free differentials in this equation refer to a segment of path along the transition curve of Fig. 5, and denote them as $dS_z, dP_z,$ and dT_z . Multiply by dT and integrate at constant pressure from one phase to the other across the transition curve in Fig. 5 to get

$$\int_P dS_z dT = 0 = -dP_z \int_P \left(\frac{\partial V}{\partial T}\right)_P dT + dT_z \int_P \left(\frac{\partial S}{\partial T}\right)_P dT. \quad (\text{A13})$$

The left side is zero since dS_z is finite and the integration region is infinitesimal. Equation (A13) gives $0 = -dP_z \Delta V + dT_z \Delta S$, which is the desired equation.

This derivation is actually the same as Gibbs'. The left side of Eq. (A13) is

$$-\int_P d \left[\left(\frac{\partial G}{\partial T}\right)_P \right]_z dT = -d \left[\int_P \left(\frac{\partial G}{\partial T}\right)_P dT \right]_z = d(G_1 - G_2)_z = 0, \quad (\text{A14})$$

which is the same as Gibbs' relation $d\mu_L = d\mu_v$ ("L" = "1," and "v" = "2"). See Eqs. (A6) and (A7), and remember $G = \mu N$. Buckingham and Fairbank in effect used an integral of a derivative of G to get the same relation obtained by Gibbs from a direct use of G .

This completes our survey. Notice from Sec. II, Nos. 7 and 8 in the Appendix that the Clausius-Clapeyron equation can be derived as a Maxwell equation for *all three* potentials $F, G,$ and H . Notice also that there is a derivation possible in which *each one* of $U, \mu, F, H, G,$ and S plays the principal role. (And it also appears in the way shown in Sec. IV.)

¹J. Willard Gibbs, *Scientific Papers* (Dover, New York, 1961), Vol. 1.

²P. Ehrenfest, *Proc. Akad. Wet.* **36**, 153 (1933); see also P. Ehrenfest,

Collected Scientific Papers (North-Holland, Amsterdam, 1959), p. 628.

³Phase transitions are discussed in every thermodynamics textbook, e.g., in M. Zemansky, *Thermodynamics* (McGraw-Hill, New York, 1981), 5th ed.

⁴W. H. Keesom, *Helium* (Elsevier, Amsterdam, 1942).

⁵We have used the data given in the comprehensive treatise by J. Wilks, *Liquid and Solid Helium* (Clarendon, Oxford, England, 1967), Appendix A1 and p. 303. We have let $C_{svp} \cong C_p$.

⁶See Ref. 4, p. 255.

⁷L. Landau, *Phys. Z. Sov.* **11**, 26, 545 (1937), updated in L. Landau and E. Lifshitz, *Statistical Physics* (Pergamon, New York, 1958), 2nd ed., pp. 430-439. Landau used for beta-brass $\eta = (p_{Cu} - p_{Zn}) / (p_{Cu} + p_{Zn})$, where p_{Cu} is the probability that a particular site is occupied by a copper atom. For a disordered state $p_{Cu} = p_{Zn}$, whence $\eta = 0$, whereas for a completely ordered state, $p_{Cu} = 1, p_{Zn} = 0$ or vice versa, whence $\eta^2 = 1$.

⁸A. B. Pippard, *The Elements of Classical Thermodynamics* (Cambridge U. P., Cambridge, England, 1957), Chap. 9.

⁹M. J. Buckingham and W. M. Fairbank, in *Progress in Low Temperature Physics*, edited by C. J. Gorter (North-Holland, Amsterdam, 1981), Vol. 3, p. 80.

¹⁰Figures 2 and 3 and the slope of the transition curve were taken from J. Wilks, *Liquid and Solid Helium* (Clarendon, Oxford, England, 1967), Appendix A1 and p. 303. (We allowed $S_{svp} \cong C_p$.)

¹¹See Ref. 7, Eq. (135.12). The two-dimensional solution is by L. Onsager.

¹²See the discussion at the end of Sec. VI.

¹³G. Ahlers, in *The Physics of Liquid and Solid Helium*, edited by K. H. Bennemann and J. B. Ketterson (Wiley, New York, 1976), Part I.

¹⁴J. C. Le Guillou and J. Zinn-Justin, *Phys. Rev. B* **21**, 3976 (1980).

¹⁵J. A. Lipa and T. C. P. Chui, *Phys. Rev. Lett.* **51**, 2291 (1987).

¹⁶D. McKie and M. H. deV. Heathcote, *The Discovery of Latent Heats* (Arnold, London, 1935), p. 20.

¹⁷The book *Reflections on the Motive Power of Fire*, edited by E. Mendoza (Dover, New York, 1960), contains the translation of Carnot's book of the same name as well as Clapeyron's and Clausius' 1850 article.

¹⁸Reference 17, p. 90.

¹⁹Reference 17, pp. 136, 137.

²⁰Lord Kelvin, *Mathematical Physics Papers I* (Cambridge U. P., Cambridge, England, 1882), pp. 232-236.

²¹Reference 1, p. 98.