

AGENDA

General thermodynamic relations

Part A: Recitation notes

1. The Clapeyron equation

We may use the Maxwell relations in a variety of ways. For example, (10.24) allows us to express the quantity h_{fg} (the enthalpy of vaporization) using P , v , and T data alone. Suppose we desire h_{fg} at the point (v_0, T_0) of Fig. 10-1. Since the temperature remains constant during the phase change, we

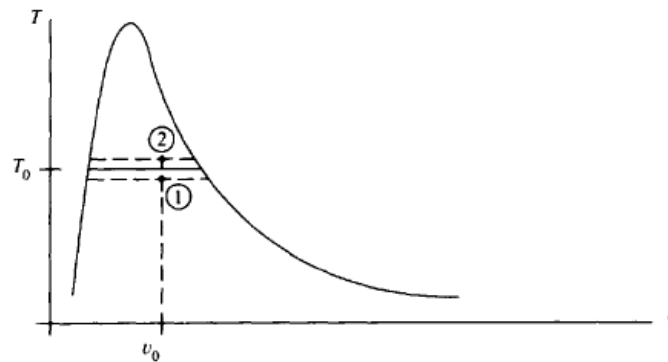


Fig. 10-1

can write

$$\left(\frac{\partial s}{\partial v}\right)_{T=T_0} = \frac{s_g - s_f}{v_g - v_f} \quad (10.26)$$

Consequently, (10.24) gives

$$\left(\frac{\partial P}{\partial T}\right)_{v=v_0} = \frac{s_{fg}}{v_{fg}} \quad (10.27)$$

But, we can integrate (10.17), knowing that P and T are constant during a phase change:

$$\int dh = \int T_0 ds - \int v dP \quad \text{or} \quad h_{fg} = T_0 s_{fg} \quad (10.28)$$

This is substituted into (10.27) to give the *Clapeyron equation*:

$$\left(\frac{\partial P}{\partial T}\right)_{v=v_0} = \frac{h_{fg}}{T_0 v_{fg}} \quad \text{or} \quad h_{fg} = T_0 v_{fg} \left(\frac{\partial P}{\partial T}\right)_{v=v_0} \quad (10.29)$$

The partial derivative $(\partial P/\partial T)_{v=v_0}$ can be evaluated from the saturated-state tables, using the central-difference approximation

$$\left(\frac{\partial P}{\partial T}\right)_{v=v_0} \cong \frac{P_2 - P_1}{T_2 - T_1} \quad (10.30)$$

where T_2 and T_1 are selected at equal intervals above and below T_0 . (See Example 10.3.)

For relatively low pressures, the Clapeyron equation can be modified when $v_g \gg v_f$. We may treat the saturated vapor as an ideal gas, so that

$$v_{fg} = v_g - v_f \cong v_g = \frac{RT}{P} \quad (10.31)$$

Then (10.29) becomes (dropping the subscript 0)

$$\left(\frac{\partial P}{\partial T}\right)_c = \frac{Ph_{fg}}{RT^2} \quad (10.32)$$

This is often referred to as the *Clausius–Clapeyron equation*. It may also be used for the sublimation process involving a solid to vapor phase change.

During a phase change, the pressure depends only on the temperature; hence, we may use an ordinary derivative so that

$$\left(\frac{\partial P}{\partial T}\right)_c = \left(\frac{dP}{dT}\right)_{\text{sat}} \quad (10.33)$$

Then (10.32) can be rearranged as

$$\left(\frac{dP}{P}\right)_{\text{sat}} = \frac{h_{fg}}{R} \left(\frac{dT}{T^2}\right)_{\text{sat}} \quad (10.34)$$

This is integrated between two saturation states to yield

$$\ln\left(\frac{P_2}{P_1}\right)_{\text{sat}} \cong \frac{h_{fg}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)_{\text{sat}} \quad (10.35)$$

where we have assumed h_{fg} to be constant between state 1 and state 2 (hence the “approximately equal to” symbol). Relationship (10.35) may be used to approximate the pressure or temperature below the limits of tabulated values (see Example 10.4).

2. General Procedure

1. The first step is to identify the variables of interest. If you have a system with only two degrees of freedom then you will have three variables, one dependent and two independent. Write down the dependent variable as a function of the two independent variables;

$$Z = Z(X, Y)$$

2. Write the total differential of Z :

$$dZ = MdX + NdY$$

where we know that the coefficients are just the partials

$$M = \left(\frac{\partial Z}{\partial X}\right)_Y$$

and

$$N = \left(\frac{\partial Z}{\partial Y}\right)_X$$

3. The third step is to convert the total differential from the independent variables of X and Y , to P and T . We do this by substituting in for dX and dY from the *Summary of Thermodynamic State Functions in terms of T and P* in the previous section. dX and dY are themselves exact differentials and so they are of the form

$$dX = \left(\frac{\partial X}{\partial P}\right)_T dP + \left(\frac{\partial X}{\partial T}\right)_P dT$$

and

$$dY = \left(\frac{\partial Y}{\partial P}\right)_T dP + \left(\frac{\partial Y}{\partial T}\right)_P dT$$

where we write $X_P = \left(\frac{\partial X}{\partial P}\right)_T$, $Y_P = \left(\frac{\partial Y}{\partial P}\right)_T$, etc. as shorthand for the partial derivatives. Notice that here that the subscripts in this notation refer to the independent variables that are *not* constant.

Then on substitution into dZ we obtain:

$$dZ = M (X_T dT + X_P dP) + N (Y_T dT + Y_P dP)$$

4. The fourth step is to collect like terms:

$$dZ = (MX_T + NY_T) dT + (MX_P + NY_P) dP$$

5. The fifth step involves writing

$$dZ = Z_T dT + Z_P dP$$

from the now obviously very useful *Summary of Thermodynamic State Functions in terms of T and P* . We now have two different expressions for $dZ(T, P)$. Since the variables T and P are both independent variables we can vary each one independent of the other and since the two expressions for dZ don't depend on the variation we know that the coefficients of dT and dP from the two expressions for dZ are equal to each other.

$$Z_T = MX_T + NY_T$$

and

$$Z_P = MX_P + NY_P$$

6. The Sixth step involves solving these two equations for M and N . Solving a system of two linear equations in two unknowns can be done by elimination of M or N and then solving for the other or by using the Jacobians of the system. For the two linear equations in the two unknowns M and N above the Jacobians are:

$$M = \frac{\begin{vmatrix} Z_T & Y_T \\ Z_P & Y_P \end{vmatrix}}{\begin{vmatrix} X_T & Y_T \\ X_P & Y_P \end{vmatrix}}$$

and

$$N = \frac{\begin{vmatrix} X_T & Z_T \\ X_P & Z_P \end{vmatrix}}{\begin{vmatrix} X_T & Y_T \\ X_P & Y_P \end{vmatrix}}$$

which of course gives you

$$M = \frac{Z_T Y_P - Z_P Y_T}{X_T Y_P - X_P Y_T}$$

and

$$N = \frac{Z_P X_T - Z_T X_P}{X_T Y_P - X_P Y_T}.$$

Part B: Questions and Answers

Question: How do you use a Jacobian?

Answer: For an in depth derivation, please refer to the lecture notes.

We generally use the Jacobian to convert a partial derivative in which the denominator and/or the constant property is not a simple parameter (T,P, or V) to a combination of derivatives with respect to T and P, which we know. The general form of the Jacobian is:

$$\left(\frac{\partial A}{\partial B}\right)_C = \frac{\begin{vmatrix} A_T & C_T \\ A_P & C_P \end{vmatrix}}{\begin{vmatrix} B_T & C_T \\ B_P & C_P \end{vmatrix}} = \frac{A_T C_P - A_P C_T}{B_T C_P - B_P C_T}$$

Where A, B, and C, are any thermodynamic state functions and $A_T = \left(\frac{\partial A}{\partial T}\right)_P$ and so on.

A_T (etc.) should be easily determined using the summary of thermodynamic relations.

Trick: Here is a very important practical trick that you can use when you need to compute a partial derivative where either T or P is fixed. For example:

$$\left(\frac{\partial V}{\partial U}\right)_T = \frac{\left(\frac{\partial V}{\partial P}\right)_T}{\left(\frac{\partial U}{\partial P}\right)_T}$$

Why is the equation (trick) above valid?

Answer: Since in both terms on the right side of the equation above T is constant, you 'may want to think' the numerator and denominator as total derivatives with respect to P, and as you know in that case, you can cancel dP (i.e. if T is constant, think of everything is a function of only P).

If you are not happy with this, here is a formal proof using the general procedure:

$$\left(\frac{\partial V}{\partial U}\right)_T = \frac{\begin{vmatrix} V_T & T_T \\ V_P & T_P \end{vmatrix}}{\begin{vmatrix} U_T & T_T \\ U_P & T_P \end{vmatrix}} = \frac{V_T T_P - V_P T_T}{U_T T_P - U_P T_T} = \frac{V_T 0 - V_P 1}{U_T 0 - U_P 1} = \frac{\left(\frac{\partial V}{\partial P}\right)_T}{\left(\frac{\partial U}{\partial P}\right)_T}$$

Note the trivial substitutions above: $T_T = \left(\frac{\partial T}{\partial T}\right)_P = 1$ and $T_P = \left(\frac{\partial T}{\partial P}\right)_T = 0$