

Chapter 7: Thermodynamic relations

- In the preceding chapters we made extensive use of the property tables.
- In this chapter, we focus our attention on how the property tables are prepared and how some unknown properties can be determined from limited available data.
- It will come as no surprise that some properties such as temperature, pressure, volume, and mass can be measured directly. Other properties such as density and specific volume can be determined from these using some simple relations.
- However, properties such as **internal energy**, **enthalpy**, and **entropy** are **not so easy to determine** because they cannot be measured directly or related to easily measurable properties through some simple relations.
- Therefore, it is essential that we develop some fundamental relations between commonly encountered thermodynamic properties and express the properties that cannot be measured directly in terms of easily measurable properties.

Partial derivatives and associated relations

- Most basic thermodynamic relations involve differentials. Therefore, we start by reviewing the derivatives and various relations among derivatives to the extent necessary in this chapter.
- Consider a function f that depends on a single variable x , that is, $f = f(x)$ as shown in figure 7.1
- The **derivative** of the function at a point defined as Slope expressed as:

$$\frac{df}{dx} = \lim_{\Delta x \rightarrow 0} \frac{\Delta f}{\Delta x} = \lim_{\Delta x \rightarrow 0} \frac{f(x + \Delta x) - f(x)}{\Delta x}$$

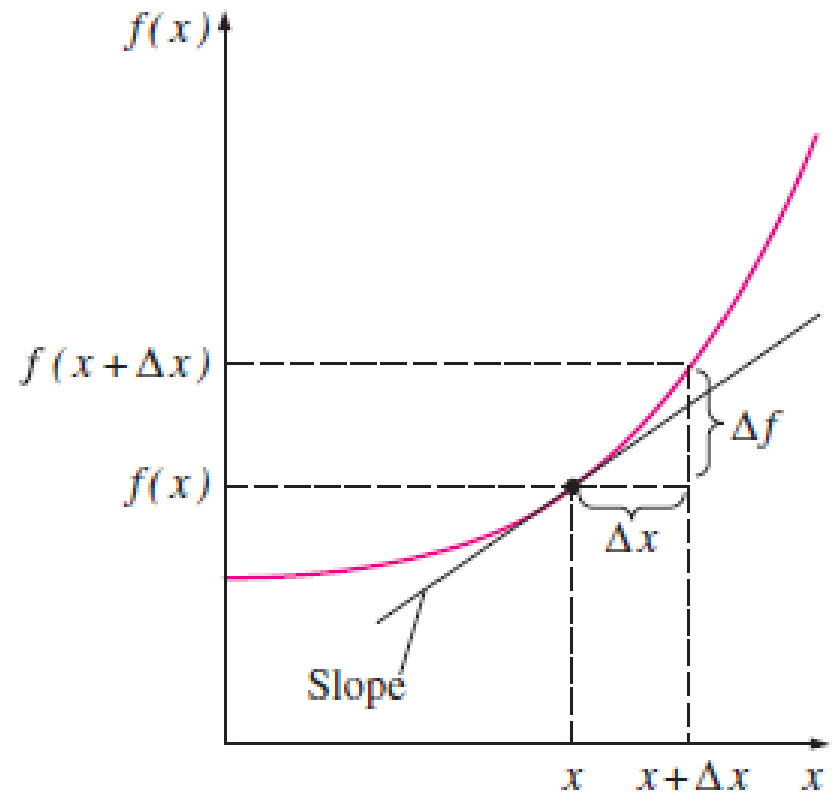


FIGURE 7.1: The derivative of a function at a specified point represents the slope of the function at that point.

- Therefore, the derivative of a function $f(x)$ with respect to x represents the rate of change of f with x .

Partial Differentials

- Now consider a function that depends on two (or more) variables, such as $z = z(x, y)$. This time the value of z depends on both x and y . It is sometimes desirable to examine the dependence of z on only one of the variables. This is done by allowing one variable to change while holding the others constant and observing the change in the function. The variation of $z(x, y)$ with x when y is held constant is called the **partial derivative** of z with respect to x , and it is expressed as

$$\left(\frac{\partial z}{\partial x}\right)_y = \lim_{\Delta x \rightarrow 0} \left(\frac{\Delta z}{\Delta x}\right)_y = \lim_{\Delta x \rightarrow 0} \frac{z(x + \Delta x, y) - z(x, y)}{\Delta x} \dots\dots\dots 7.2$$

- To obtain a relation for the total differential change in $z(x, y)$ for simultaneous changes in x and y would be:

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \dots\dots\dots 7.3$$

Cont...

- Equation 7.3 is the fundamental relation for the **total differential** of a dependent variable in terms of its partial derivatives with respect to the independent variables. This relation can easily be extended to include more independent variables.

EXAMPLE 1: see on page 654

Partial Differential Relations

- Now let us rewrite Eq. 7.3 as:

$$dz = M dx + N dy \quad \dots\dots\dots 7.4$$

where

$$M = \left(\frac{\partial z}{\partial x} \right)_y \quad \text{and} \quad N = \left(\frac{\partial z}{\partial y} \right)_x$$

- Taking the partial derivative of M with respect to y and of N with respect to x yields

$$\left(\frac{\partial M}{\partial y} \right)_x = \frac{\partial^2 z}{\partial x \partial y} \quad \text{and} \quad \left(\frac{\partial N}{\partial x} \right)_y = \frac{\partial^2 z}{\partial y \partial x}$$

Cont...

- Therefore, the two relations above are identical:

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \quad \dots\dots\dots 7.5$$

- This is an important relation for partial derivatives, and it is used in calculus to test whether a differential dz is **exact** or **inexact**. In thermodynamics, this relation forms the basis for the development of the **Maxwell relations** discussed in the next section.
- Finally, we develop **two important relations** for partial derivatives—the **reciprocity** and the **cyclic relations**.
 - ✓ The function $z = z(x, y)$ can also be expressed as $x = x(y, z)$ if y and z are taken to be the **independent variables**. Then the total differential of x becomes, from Eq. 7.3:

$$dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz \quad \dots\dots\dots 7.6$$

- Eliminating dx by combining Eqs. 7.3 and 7.6, we have

$$dz = \left[\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z + \left(\frac{\partial z}{\partial y}\right)_x \right] dy + \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial x}\right)_y dz$$

Cont...

- Rearranging would give

$$\left[\left(\frac{\partial z}{\partial x} \right)_y \left(\frac{\partial x}{\partial y} \right)_z + \left(\frac{\partial z}{\partial y} \right)_x \right] dy = \left[1 - \left(\frac{\partial x}{\partial z} \right)_y \left(\frac{\partial z}{\partial x} \right)_y \right] dz \quad \dots\dots\dots 7.7$$

- The variables y and z are independent of each other and thus can be varied independently. For example, y can be held constant ($dy = 0$), and z can be varied over a range of values ($dz \neq 0$). Therefore, for this equation to be valid at all times, the terms in the brackets must equal zero, regardless of the values of y and z . Setting the terms in each bracket equal to zero gives

$$\left(\frac{\partial x}{\partial z} \right)_y \left(\frac{\partial z}{\partial x} \right)_y = 1 \rightarrow \left(\frac{\partial x}{\partial z} \right)_y = \frac{1}{(\partial z / \partial x)_y} \quad \dots\dots\dots 7.8$$

$$\left(\frac{\partial z}{\partial x} \right)_y \left(\frac{\partial x}{\partial y} \right)_z = - \left(\frac{\partial x}{\partial y} \right)_x \rightarrow \left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial z} \right)_x \left(\frac{\partial z}{\partial x} \right)_y = -1 \quad \dots\dots\dots 7.9$$

Cont...

- The first relation is called the **reciprocity relation**, and it shows that the inverse of a partial derivative is equal to its reciprocal (Fig. 7.2). The second relation is called the **cyclic relation**, and it is frequently used in thermodynamics.

$$\begin{aligned} &\text{Function: } z + 2xy - 3y^2z = 0 \\ &1) \quad z = \frac{2xy}{3y^2 - 1} \rightarrow \left(\frac{\partial z}{\partial x} \right)_y = \frac{2y}{3y^2 - 1} \\ &2) \quad x = \frac{3y^2z - z}{2y} \rightarrow \left(\frac{\partial x}{\partial z} \right)_y = \frac{3y^2 - 1}{2y} \\ &\text{Thus, } \left(\frac{\partial z}{\partial x} \right)_y = \frac{1}{\left(\frac{\partial x}{\partial z} \right)_y} \end{aligned}$$

FIGURE 7.2: Demonstration of the reciprocity relation for the function $z + 2xy - 3y^2z = 0$

The maxwell relations

- The equations that relate the partial derivatives of properties P , v , T , and s of a simple compressible system to each other are called the **Maxwell relations**. They are obtained from the **four Gibbs equations** by exploiting the exactness of the differentials of thermodynamic properties.
- **Two** of the **Gibbs relations** were derived in Chapter 7 (i.e., when you are dealing Entropy in thermo I) and expressed as:

$$du = T ds - P dv \quad \text{.....7.10}$$

$$dh = T ds + v dP \quad \text{.....7.11}$$

- The other **two Gibbs relations** are based on two new combination properties— the **Helmholtz function** a and the **Gibbs function** g , defined as:

$$a = u - Ts \quad \text{.....7.12}$$

$$g = h - Ts \quad \text{.....7.13}$$

Differentiating, we get

$$da = du - T ds - s dT$$

$$dg = dh - T ds - s dT$$

Cont...

- Simplifying the above relations by using Eqs. 7.10 and 7.11, we obtain the other two Gibbs relations for simple compressible systems:

$$da = -s dT - P dv \quad \text{.....7.14}$$

$$dg = -s dT + v dP \quad \text{.....7.15}$$

- A careful examination of the **four Gibbs relations** (i.e., equation 7.10, 7.11, 7.14 and 7.15) reveals that they are of the form

$$dz = M dx + N dy \quad \text{.....7.4}$$

$$\text{With} \quad \left(\frac{\partial M}{\partial y} \right)_x = \left(\frac{\partial N}{\partial x} \right)_y \quad \text{.....7.5}$$

since u , h , a , and g are properties and thus have exact differentials. Applying Eq. 7.5 to each of them, we obtain

$$\left(\frac{\partial T}{\partial v} \right)_s = - \left(\frac{\partial P}{\partial s} \right)_v \quad \text{.....7.16}$$

$$\left(\frac{\partial s}{\partial v} \right)_T = \left(\frac{\partial P}{\partial T} \right)_v \quad \text{.....7.18}$$

$$\left(\frac{\partial T}{\partial P} \right)_s = \left(\frac{\partial v}{\partial s} \right)_P \quad \text{.....7.17}$$

$$\left(\frac{\partial s}{\partial P} \right)_T = - \left(\frac{\partial v}{\partial T} \right)_P \quad \text{.....7.19}$$

Equation 7.16 to 7.19 are called the **Maxwell relations**

Cont...

- The Maxwell relations are extremely valuable in thermodynamics because they provide a means of determining the **change in entropy**, which **cannot be measured directly**, by simply measuring the changes in properties P , v , and T . Note that the Maxwell relations given above are **limited to simple compressible systems**. However, other similar relations can be written just as easily for non-simple systems such as those involving electrical, magnetic, and other effects.
- ***EXAMPLE: on page 658***

The Clapeyron equation

- The Maxwell relations have far-reaching implications in thermodynamics and are frequently used to derive useful thermodynamic relations.
- The Clapeyron equation is one such relation, and it enables us to determine the **enthalpy change** associated with a **phase change** (such as the enthalpy of vaporization h_{fg}) from a knowledge of P , v , and T data alone. Consider the third Maxwell relation, Eq. 7.18:

$$\left(\frac{\partial P}{\partial T} \right)_v = \left(\frac{\partial s}{\partial v} \right)_T$$

- During a phase-change process, **the pressure** is the **saturation pressure**, which depends on **the temperature only** and is independent of the **specific volume**

That is, $P_{\text{sat}} = f(T_{\text{sat}})$.

- Therefore, the partial derivative $(\partial P / \partial T)_v$ can be expressed as a total derivative $(dP/dT)_{\text{sat}}$, which is the slope of the saturation curve on a P - T diagram at a specified saturation state (Fig. 7.3). This slope is independent of the specific volume, and thus it can be treated as a constant during the integration of Eq. 7.18 between two saturation states at the same temperature. For an isothermal liquid–vapor phase-change process, for example, the integration yields

Cont...

$$s_g - s_f = \left(\frac{dP}{dT} \right)_{\text{sat}} (v_g - v_f) \dots\dots\dots 7.20$$

Rearranging would give

$$\left(\frac{dP}{dT} \right)_{\text{sat}} = \frac{s_{fg}}{v_{fg}} \dots\dots\dots 7.21$$

During this process the pressure also remains constant. Therefore, from Eq. 7.11,

$$dh = T ds + v dP \xrightarrow{0}$$

$$\int_f^g dh = \int_f^g T ds \rightarrow h_{fg} = T s_{fg}$$

Substituting this result into Eq. 7.21, we obtain

$$\left(\frac{dP}{dT} \right)_{\text{sat}} = \frac{h_{fg}}{T v_{fg}} \dots\dots\dots 7.22$$

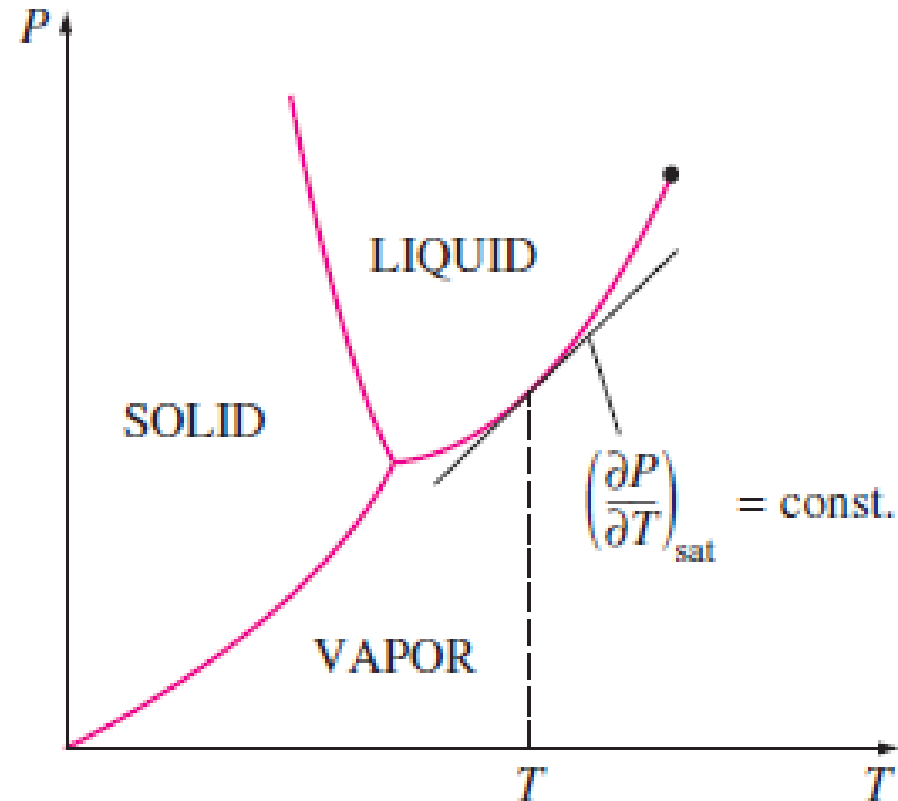


FIGURE 7.3: The slope of the saturation curve on a P - T diagram is constant at a constant T or P .

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- Equation 7.22 is called the **Clapeyron equation** after the French engineer and physicist E. Clapeyron (1799–1864). This is an important thermodynamic relation since it enables us to determine the **enthalpy of vaporization** h_{fg} at a given temperature by simply measuring the slope of the saturation curve on a P - T diagram and the specific volume of saturated liquid and saturated vapor at the given temperature.
- The Clapeyron equation is applicable to any phase-change process that occurs at constant temperature and pressure. It can be expressed in a general form as

$$\left(\frac{dP}{dT} \right)_{\text{sat}} = \frac{h_{12}}{Tv_{12}} \quad \text{..... 7.23}$$

where the subscripts 1 and 2 indicate the two phases.

EXAMPLE: on page 659

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- The Clapeyron equation can be simplified for **liquid–vapor** and **solid–vapor** phase changes by utilizing some approximations. At low pressures $v_g \gg v_f$, and thus $v_{fg} \approx v_g$. By treating the vapor as an ideal gas, we have $v_g = RT/P$. Substituting these approximations into Eq. 7.22, we find

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

For small temperature intervals h_{fg} can be treated as a constant at some average value. Then integrating this equation between two saturation states yields

$$\ln\left(\frac{P_2}{P_1}\right)_{\text{sat}} \cong \frac{h_{fg}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)_{\text{sat}} \quad \dots\dots\dots 7.24$$

This equation is called the **Clapeyron–Clausius equation**, and it can be used to determine the variation of saturation pressure with temperature. It can also be used in the solid–vapor region by replacing h_{fg} by h_{ig} (the enthalpy of sublimation) of the substance.

General relations for du , dh , ds , C_v , and C_p

- The state postulate established that the state of a simple compressible system is completely specified by two independent, intensive properties. Therefore, at least theoretically, we should be able to calculate all the properties of a system at any state once two independent, intensive properties are available. This is certainly good news for properties that cannot be measured directly such as internal energy, enthalpy, and entropy. However, the calculation of these properties from measurable ones depends on the availability of simple and accurate relations between the two groups.
- In this section we develop general relations for changes in internal energy, enthalpy, and entropy in terms of pressure, specific volume, temperature, and specific heats alone. We also develop some general relations involving specific heats. The relations developed will enable us to determine the *changes* in these properties. The property values at specified states can be determined only after the selection of a reference state, the choice of which is quite arbitrary.

Internal Energy Changes

- We choose the internal energy to be a function of T and v ; that is, $u = u(T, v)$ and take its total differential (Applying Eq. 7-3):

$$du = \left(\frac{\partial u}{\partial T} \right)_v dT + \left(\frac{\partial u}{\partial v} \right)_T dv$$

Using the definition of C_v , we have

$$du = c_v dT + \left(\frac{\partial u}{\partial v} \right)_T dv \quad \dots\dots\dots 7.25$$

Now we choose the **entropy** to be a function of T and v ; that is, $s = s(T, v)$ and take its total differential,

$$ds = \left(\frac{\partial s}{\partial T} \right)_v dT + \left(\frac{\partial s}{\partial v} \right)_T dv \quad \dots\dots\dots 7.26$$

Substituting this into the $T ds$ relation $du = T ds - P dv$ yields

$$du = T \left(\frac{\partial s}{\partial T} \right)_v dT + \left[T \left(\frac{\partial s}{\partial v} \right)_T - P \right] dv \quad \dots\dots\dots 7.27$$

Cont...

Equating the coefficients of dT and dv in Eqs. 7.25 and 7.27 gives

$$\left(\frac{\partial s}{\partial T}\right)_v = \frac{c_v}{T}$$
$$\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial s}{\partial v}\right)_T - P \quad \dots\dots\dots 7.28$$

Using the third Maxwell relation (Eq. 7.18), we get

$$\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_v - P$$

Substituting this into Eq. 7.25, we obtain the desired relation for du :

$$du = c_v dT + \left[T\left(\frac{\partial P}{\partial T}\right)_v - P \right] dv \quad \dots\dots\dots 7.29$$

The change in internal energy of a simple compressible system associated with a change of state from (T_1, v_1) to (T_2, v_2) is determined by integration:

$$u_2 - u_1 = \int_{T_1}^{T_2} c_v dT + \int_{v_1}^{v_2} \left[T\left(\frac{\partial P}{\partial T}\right)_v - P \right] dv \quad \dots\dots\dots 7.30$$

Enthalpy Changes

- The general relation for dh is determined in exactly the same manner. This time we choose the enthalpy to be a function of T and P , that is, $h = h(T, P)$, and take its total differential,

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

Using the definition of C_p , we have

$$dh = c_p dT + \left(\frac{\partial h}{\partial P} \right)_T dP \quad \dots\dots\dots 7.31$$

Now we choose the entropy to be a function of T and P ; that is, we take $s = s(T, P)$ and take its total differential,

$$ds = \left(\frac{\partial s}{\partial T} \right)_P dT + \left(\frac{\partial s}{\partial P} \right)_T dP \quad \dots\dots\dots 7.32$$

Substituting this into the $T ds$ relation $dh = T ds + v dP$ gives

$$dh = T \left(\frac{\partial s}{\partial T} \right)_P dT + \left[v + T \left(\frac{\partial s}{\partial P} \right)_T \right] dP \quad \dots\dots\dots 7.33$$

Equating the coefficients of dT and dP in Eqs. 7.31 and 7.33, we obtain

Cont...

$$\left(\frac{\partial s}{\partial T}\right)_P = \frac{c_p}{T}$$

$$\left(\frac{\partial h}{\partial P}\right)_T = v + T\left(\frac{\partial s}{\partial P}\right)_T \quad \dots\dots\dots 7.34$$

Using the fourth Maxwell relation (Eq. 7.19), we have

$$\left(\frac{\partial h}{\partial P}\right)_T = v - T\left(\frac{\partial v}{\partial T}\right)_P$$

Substituting this into Eq. 7.31, we obtain the desired relation for dh :

$$dh = c_p dT + \left[v - T\left(\frac{\partial v}{\partial T}\right)_P \right] dP \quad \dots\dots\dots 7.35$$

The change in enthalpy of a simple compressible system associated with a change of state from (T_1, P_1) to (T_2, P_2) is determined by integration:

$$h_2 - h_1 = \int_{T_1}^{T_2} c_p dT + \int_{P_1}^{P_2} \left[v - T\left(\frac{\partial v}{\partial T}\right)_P \right] dP \quad \dots\dots\dots 7.36$$

In reality, one needs only to determine either $(u_2 - u_1)$ from Eq. 7.30 or $(h_2 - h_1)$ from Eq. 7.36, depending on which is more suitable to the data at hand. The other can easily be determined by using the definition of enthalpy $h = u + Pv$:

$$h_2 - h_1 = u_2 - u_1 + (P_2 v_2 - P_1 v_1) \quad \dots\dots\dots 7.37$$

Entropy Changes

- here we develop **two general relations** for the **entropy change of a simple compressible system**.

- ✓ The first relation is obtained by replacing the first partial derivative in the total differential ds (Eq. 7.26) by Eq. 7.28 and the second partial derivative by the third Maxwell relation (Eq. 7.18), yielding

$$ds = \frac{c_v}{T} dT + \left(\frac{\partial P}{\partial T} \right)_v dv \quad \dots\dots\dots 7.38$$

Up on integration, we get

$$s_2 - s_1 = \int_{T_1}^{T_2} \frac{c_v}{T} dT + \int_{v_1}^{v_2} \left(\frac{\partial P}{\partial T} \right)_v dv \quad \dots\dots\dots 7.39$$

- ✓ The second relation is obtained by replacing the first partial derivative in the total differential of ds (Eq. 7.32) by Eq. 7.34, and the second partial derivative by the fourth Maxwell relation (Eq. 7.19), yielding

$$ds = \frac{c_p}{T} dT - \left(\frac{\partial v}{\partial T} \right)_p dP \quad \dots\dots\dots 7.40 \quad \text{Up on integration, we get}$$

$$s_2 - s_1 = \int_{T_1}^{T_2} \frac{c_p}{T} dT - \int_{P_1}^{P_2} \left(\frac{\partial v}{\partial T} \right)_p dP \quad \dots\dots\dots 7.41$$

Either relation can be used to determine the entropy change. The proper choice depends on the available data.

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