

Chap. 7 Thermodynamic Relations

7.1 Exact differentials	1
7.2 The Maxwell Relations and other Useful Formulas.....	4
7.3 Thermodynamic Relations for Nonideal Behavior	6
Internal Energy and Enthalpy	6
Entropy.....	7
Heat Capacities	8
7.4 Relations for nonideal gases with special process restraints.....	11
Isentropic process	11
Joule Expansion (constant internal energy process)	13
The Joule-Thomson Coefficient (constant enthalpy process).....	14

Of all the thermodynamic properties that have been introduced in the preceding chapters, only a few can be directly measured by laboratory experiments. Pressure, temperature and volume are obviously among the measurable properties. However, there is no instrument to measure entropy or any of the properties related to energy (u , h , f , and g). These quantities cannot be assigned absolute values^{*}; only changes in them as a result of a process have quantitative meaning. All of the thermodynamic information concerning simple substances (i.e., one-component systems) is based upon measurements of the equation of state $v(p,T)$, the temperature-dependent heat capacity $C_p(T)$ at a particular pressure, and the enthalpy changes associated with phase transitions.

One of the significant achievements of classical thermodynamics is its ability to provide connections between various properties, so that only a few measurements are needed for a complete description of a substance. For example, the difference between the specific heats and the effect of pressure on the enthalpy can be obtained if the p - v - T equation of state of the substance is known. For the ideal gas and the approximate model of condensed phases presented in Chap. 2, there was no need for a formalized approach to these relations; to continue the above example, $C_p - C_v$ is equal to the gas constant R for an ideal gas and is approximately zero for solids and liquids; for most applications, the enthalpy of any substance can be assumed to be independent of pressure.

For a more accurate description, particularly for nonideal gases and condensed phases under extreme conditions, the relationships between thermodynamic properties need to be developed. Establishing these connections is the purpose of the present chapter. First, certain mathematical fundamentals need to be reviewed. These are based on the fact that all thermodynamic properties of a particular phase of a simple substance are smoothly-varying functions of any two other thermodynamic properties.

7.1 Exact differentials

For a simple substance, the phase rule requires that specification of any two properties, say x and y , determines all other properties. Denoting one of the dependent properties by z , the relation between the three is written as $z(x,y)$. The relations between x , y , and z and other thermodynamic properties are derived from the *total differential* of z , which is:

$$dz = \left(\frac{\partial z}{\partial x} \right)_y dx + \left(\frac{\partial z}{\partial y} \right)_x dy = M(x,y)dx + N(x,y)dy \quad (7.1)$$

The partial derivatives depend on x and y as expressed by the functions M and N in the second equality of Eq (7.1):

$$M(x,y) = \left(\frac{\partial z}{\partial x} \right)_y \quad N(x,y) = \left(\frac{\partial z}{\partial y} \right)_x \quad (7.2)$$

^{*} except for entropy, which according to the Third law, is zero at 0 K.

Total differentials have the mathematical characteristic of being *exact* or *inexact*. The distinction is determined by comparison of the mixed second derivatives of z :

$$\left(\frac{\mathcal{M}}{\mathcal{N}}\right)_x = \left[\frac{\mathcal{I}}{\mathcal{Y}}\left(\frac{\mathcal{K}}{\mathcal{K}}\right)_y\right]_x \quad \left(\frac{\mathcal{N}}{\mathcal{K}}\right)_y = \left[\frac{\mathcal{I}}{\mathcal{K}}\left(\frac{\mathcal{Y}}{\mathcal{Y}}\right)_x\right]_y \quad (7.3)$$

The total differential is exact if the order of forming the mixed second derivative is immaterial, or if:

$$\left(\frac{\mathcal{N}}{\mathcal{K}}\right)_y = \left(\frac{\mathcal{M}}{\mathcal{Y}}\right)_x \quad (7.4)$$

A mathematical corollary of the exactness property of a total differential is that its integral $z_2 - z_1$ from state 1 to state 2 [i.e., for the process from (x_1, y_1) to (x_2, y_2)] is independent of the path, which can be described by a function $y = F(x)$. For example, if x and y denote p and T , the path could be a combination of an isothermal step and an isobaric step. Or, x and y could vary in a continuous fashion as shown by the curve $y = F(x)$ on the $x - y$ plane in Fig. 7.1. This curve generates a corresponding path on the $z(x, y)$ surface, as shown in the diagram. If y is eliminated from Eq (7.1) using $y = F(x)$,

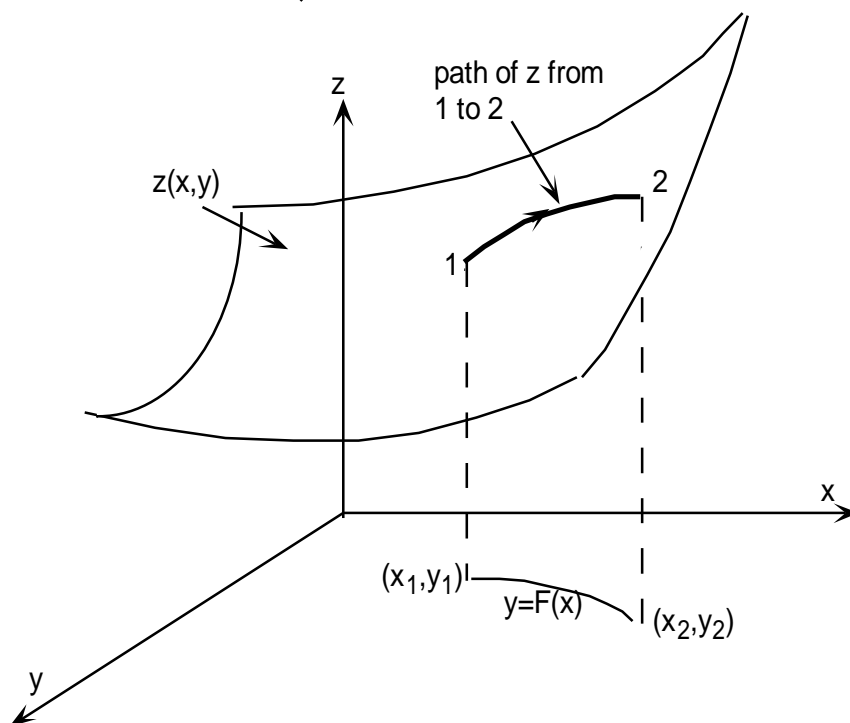


Fig. 7.1 Path of a process that changes a simple substance from state 1 to state 2

the total differential can be integrated from state 1 to state 2 to yield:

$$z_2 - z_1 = \int_{x_1}^{x_2} \left\{ M[x, F(x)] + N[x, F(x)] \frac{dF}{dx} \right\} dx \quad (7.5)$$

If the total differential is exact, Eq (7.4) is satisfied and Eq (7.5) gives the same value of $z_2 - z_1$ for all paths $F(x)$. Problem 7.1 provides a purely mathematical exercise to help understand the distinction between exact and inexact differentials.

The relevance of the above mathematical prelude to thermodynamics stems from the independence of thermodynamic property changes on the path of a process. This characteristic implies that all thermodynamic functions also must satisfy Eq (7.4). It applies when M and N are partial derivatives of particular properties (as in Eq (7.2)) and, more generally, when M and N are *any* functions of thermodynamic properties.

The total differential of Eq (7.1) can be manipulated to produce relationships between partial derivatives of x, y, and z, or other variables. The technique can be described as the “divide-and-hold-constant” method. It works as follows: Eq (7.1) is divided by one of the differentials and a different one is required to be zero (thus holding constant the variable associated with it). For example, suppose Eq (7.1) is divided by dy with z held constant (i.e., $dz = 0$). The result is the following relation:

$$0 = \left(\frac{\mathcal{F}_k}{\mathcal{F}_k} \right)_y \left(\frac{\mathcal{F}_k}{\mathcal{F}_y} \right)_z + \left(\frac{\mathcal{F}_k}{\mathcal{F}_y} \right)_x$$

or, because partial derivatives can be inverted, the above equation becomes what is called the *cyclic transformation*:

$$\left(\frac{\mathcal{F}_k}{\mathcal{F}_y} \right)_z \left(\frac{\mathcal{F}_y}{\mathcal{F}_k} \right)_x \left(\frac{\mathcal{F}_k}{\mathcal{F}_k} \right)_y = -1 \quad (7.6)$$

In another example of the “divide-and-hold-constant” method, Eq (7.1) can be divided by a fourth variable w with x held constant to yield:

$$\left(\frac{\mathcal{F}_k}{\mathcal{F}_w} \right)_x = \left(\frac{\mathcal{F}_k}{\mathcal{F}_y} \right)_x \left(\frac{\mathcal{F}_y}{\mathcal{F}_w} \right)_x \quad (7.7)$$

which is the *chain rule* for partial derivatives.

It is obvious that there are so many combinations of variables in the “divide-and-hold-constant” method that attempting to construct an exhaustive catalog of relations such

as Eqs (7.6) and (7.7) would be fruitless. The practical approach is to apply the method to suit the needs of particular problems.

Example: If a fluid is heated in a constant-volume container from T to $T + \Delta T$, what is the pressure rise Δp ?

For this problem, the starting function is the equation of state $v(T,p)$, for which the total differential is:

$$dv = \left(\frac{\partial v}{\partial T} \right)_p dT + \left(\frac{\partial v}{\partial p} \right)_T dp$$

Dividing by dT and holding v constant produces the analog of Eq (7.6), written as:

$$\left(\frac{\partial p}{\partial T} \right)_v = - \frac{(\partial v / \partial T)_p}{(\partial v / \partial p)_T} = \frac{a}{b} \quad (7.8)$$

where α and β are the coefficients of thermal expansion and isothermal compressibility, respectively (see Eq (1.2)). If these coefficients are substantially constant over the range of T and p involved, Eq (7.8) can be directly integrated to yield:

$$\Delta p = \frac{a}{b} \Delta T$$

7.2 The Maxwell Relations and other Useful Formulas

The fundamental differentials described in section 2 of Chap.5 are of the form of Eq (7.1). They provide the starting point for obtaining many useful thermodynamic relations. The fundamental differentials are represented as the exact differential of $u(s,v)$, $h(s,p)$, $f(T,v)$, and $g(T,p)$:

$$du = \left(\frac{\partial u}{\partial s} \right)_v ds + \left(\frac{\partial u}{\partial v} \right)_s dv = Tds - pdv \quad (7.9)$$

$$dh = \left(\frac{\partial h}{\partial s} \right)_p ds + \left(\frac{\partial h}{\partial p} \right)_s dp = Tds + vdp \quad (7.10)$$

$$df = \left(\frac{\partial f}{\partial T} \right)_v dT + \left(\frac{\partial f}{\partial v} \right)_T dv = -sdT - pdv \quad (7.11)$$

$$dg = \left(\frac{\partial g}{\partial T} \right)_p dT + \left(\frac{\partial g}{\partial p} \right)_T dp = -sdT + vdp \quad (7.12)$$

Note that each of the energy-like properties has a pair of “natural” variables associated with it. The variables in each pair are those that appear in the fundamental differential for

the particular property. However, these associations are not fixed; it is possible, for example, to assume u to be a function of p and T and write the total differential du based on these variables instead of the “natural” pair s and v .

Equating the coefficients of the differentials in Eqs (7.9) - (7.12) produces eight useful thermodynamic relations:

$$\left(\frac{\mathcal{H}u}{\mathcal{H}v}\right)_v = \left(\frac{\mathcal{H}h}{\mathcal{H}p}\right)_p = T \quad (7.13)$$

$$\left(\frac{\mathcal{H}u}{\mathcal{H}v}\right)_s = \left(\frac{\mathcal{H}f}{\mathcal{H}v}\right)_T = -p \quad (7.14)$$

$$\left(\frac{\mathcal{H}h}{\mathcal{H}p}\right)_s = \left(\frac{\mathcal{H}g}{\mathcal{H}p}\right)_T = v \quad (7.15)$$

$$\left(\frac{\mathcal{H}f}{\mathcal{H}T}\right)_v = \left(\frac{\mathcal{H}g}{\mathcal{H}T}\right)_p = -s \quad (7.16)$$

A most useful foursome of thermodynamic relations is obtained by noting that the form of the fundamental differentials of Eqs (7.9) - (7.12) is the same as the total differential of Eq (7.1). Consisting solely of thermodynamic properties, the fundamental differentials are exact (in the mathematical sense defined earlier). Hence, Eq (7.9) applies to them. For example, for the fundamental differential $du = Tds - pdv$, the correspondence with the general formula sets $M = T$, $N = -p$, $x = s$, and $y = v$. With these variables, Eq (7.4) gives:

$$\left(\frac{\mathcal{H}T}{\mathcal{H}v}\right)_s = -\left(\frac{\mathcal{H}p}{\mathcal{H}v}\right)_v \quad (7.17)$$

The remaining fundamental differentials in Eqs (7.10) - (7.12) yield:

$$\left(\frac{\mathcal{H}T}{\mathcal{H}p}\right)_s = \left(\frac{\mathcal{H}v}{\mathcal{H}p}\right)_p \quad (7.18)$$

$$\left(\frac{\mathcal{H}p}{\mathcal{H}v}\right)_T = \left(\frac{\mathcal{H}p}{\mathcal{H}T}\right)_v \quad (7.19)$$

$$\left(\frac{\mathcal{H}p}{\mathcal{H}p}\right)_T = -\left(\frac{\mathcal{H}v}{\mathcal{H}T}\right)_p \quad (7.20)$$

Equations (7.17) - (7.20) are collectively known as the *Maxwell relations*. In the following sections, these relations, together with the fundamental differentials and Eqs (7.13) - (7.16), will be utilized to derive a number of useful relationships between the thermodynamic properties of simple substances.

7.3 Thermodynamic Relations for Nonideal Behavior

In Chapters 2 and 3, numerous property relations were presented for ideal gas and idealized solids. The latter are characterized by constant coefficients of thermal expansion and compressibility and obey the equation of state given by Eq (2.16). For these substances,

- the specific heats (and hence the internal energy and enthalpy) are functions of temperature but are independent of pressure or specific volume
- the entropy of the ideal gas varies with T and v (or p) according to Eqs (3.9) and (3.10). The entropy of the idealized solid is much more sensitive to temperature than to pressure
- For an ideal gas, the difference between C_p and C_v is equal to the gas constant. For the ideal solid, C_p is just slightly larger than C_v .

While the simplified representations above are reasonably applicable for most materials at moderate pressures and temperatures, more exact descriptions are occasionally needed. The objective of this section is to express the deviations from ideality in terms of the equation of state of the substance and its heat capacity. Basically, we seek to write total differentials of du, dh and ds in terms of p, v, and T, and of C_p or C_v .

Internal Energy and Enthalpy

Consider the internal energy to be a function of temperature and specific volume, or $u(T,v)$. The total differential is:

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

The coefficient of dT is by definition the heat capacity at constant volume, C_v . The coefficient of dv is obtained from the fundamental differential $du = Tds - pdv$ by dividing by dv and holding T constant:

$$\left(\frac{\partial u}{\partial v} \right)_T = T \left(\frac{\partial s}{\partial v} \right)_T - p = T \left(\frac{\partial p}{\partial T} \right)_v - p \quad (7.21a)$$

Where the partial derivative involving the entropy has been replaced by the Maxwell relation of Eq (7.19). The final result for du is:

$$du = C_v dT + \left[T \left(\frac{\partial p}{\partial T} \right)_v - p \right] dv \quad (7.21b)$$

This form is useful for nonideal gases for which an equation of state $p(T,v)$ is available. For solids, replacement of $(\partial p/\partial T)_v$ by α/β (see Eq (7.8)) provides a more useful form.

The relation analogous to Eq (7.21a) for the enthalpy is obtained from the total differential of $h(T,p)$ and following a procedure similar to that used above for the internal energy. The fundamental differential $dh = Tds + vdp$ is divided by dp at constant T to arrive at $(\partial h/\partial p)_T$ in terms of $(\partial s/\partial p)_T$, which is then eliminated by the Maxwell relation given by Eq (7.20). The result is:

$$\left(\frac{\partial h}{\partial p} \right)_T = T \left(\frac{\partial s}{\partial p} \right)_T + v = -T \left(\frac{\partial v}{\partial T} \right)_p + v \quad (7.22a)$$

The total differential of h is:

$$dh = C_p dT + \left[v - T \left(\frac{\partial v}{\partial T} \right)_p \right] dp \quad (7.22b)$$

For solids, substitution of αv for the partial derivative is preferred.

For an ideal gas, the bracketed terms in Eqs (7.21b) and (7.22b) are identically zero. For solids, the entire second terms on the right hand sides of these equations, when integrated over v or p , are generally small compared to $\int C_v dT$ or $\int C_p dT$.

Other derivatives of the internal energy and enthalpy can be obtained by different manipulations of the fundamental differentials of du and dh from those employed above to give Eqs (7.21a) and (7.22a). Problem 7.2 applies this method to the derivatives $(\partial u/\partial p)_T$ and $(\partial u/\partial T)_p$, wherein the “off-natural” variable p replaces the “natural” variable v associated with u (see Sect. 7.2). However, there are practical situations in which the off-natural derivatives are important. Problem 7.3 shows that $(\partial u/\partial p)_T$ can be obtained in three different ways. (in thermodynamics, there is often more than one way to skin a cat). This quantity is then applied to calculate the internal energy change caused by isothermal compression of a solid by 100 atm. The effect is equivalent to the Δu produced by a temperature increase of less than 1°C.

For an ideal gas, internal energy and enthalpy are independent of system volume or pressure. For a nonideal gas such as one obeying the Van der Waals equation of state, both u and h depend on volume, as shown in Problem 7.4

Entropy

For the entropy expressed as $s(T,v)$, the total differential is:

$$ds = \left(\frac{\mathcal{J}s}{\mathcal{J}T} \right)_v dT + \left(\frac{\mathcal{J}s}{\mathcal{J}v} \right)_T dv \quad (7.23a)$$

The coefficient of dT is C_v/T , as can be demonstrated from $du = Tds - pdv$ by dividing by dT while holding v constant. The coefficient of dv is eliminated using the Maxwell relation Eq (7.19), leading to the final result:

$$ds = \frac{C_v}{T} dT + \left(\frac{\mathcal{J}p}{\mathcal{J}T} \right)_v dv \quad (7.23b)$$

Starting from $s(T,p)$ yields an alternative entropy differential:

$$ds = \left(\frac{\mathcal{J}s}{\mathcal{J}T} \right)_p dT + \left(\frac{\mathcal{J}s}{\mathcal{J}p} \right)_T dp \quad (7.24a)$$

The fundamental differential $dh = Tds + vdp$ gives C_p/T as the coefficient of dT and use of the Maxwell relation Eq (7.20) gives the coefficient of dp . The end result is:

$$ds = \frac{C_p}{T} dT - \left(\frac{\mathcal{J}v}{\mathcal{J}T} \right)_p dp \quad (7.24b)$$

When integrated for an ideal gas with constant heat capacity, Eqs (7.23b) and (7.24b) reduce to Eqs (3.9) and (3.10), respectively. The first pair of equations apply to any one-component substance, but to integrate them, a path $v = F(T)$ or $p = G(T)$ must be specified. The resulting change in entropy, however, is independent of the path chosen.

For solids, the coefficients of dv in Eq (7.23b) and dp in Eq (7.24b) are best replaced by α/β and αv , respectively.

Equations (7.23b) and (7.24b) are sometimes called the two “ds” equations. There is a third variant in which the independent variables are p and v . This equation is given in problem 7.7 and derived in this exercise.

Heat Capacities

Subtracting Eq (7.23b) from Eq (7.24b) gives:

$$(C_p - C_v)dT = T \left(\frac{\mathcal{J}v}{\mathcal{J}T} \right)_p dp + T \left(\frac{\mathcal{J}p}{\mathcal{J}T} \right)_v dv$$

Dividing by dv and holding p constant gives:

$$(C_p - C_v) \left(\frac{\mathcal{J}T}{\mathcal{J}v} \right)_p = T \left(\frac{\mathcal{J}p}{\mathcal{J}T} \right)_v$$

Inverting the partial derivative on the left hand side yields:

$$C_p - C_v = T \left(\frac{\mathcal{J}v}{\mathcal{J}T} \right)_p \left(\frac{\mathcal{J}p}{\mathcal{J}T} \right)_v = \frac{\mathbf{a}^2 T v}{\mathbf{b}} \quad (7.25)$$

The first equality is used for gases and the second for condensed phases. For an ideal gas, the product of T and the two partial derivatives is equal to the gas constant. For nonideal gases, on the other hand, the two heat capacities can differ significantly from R (see problem 7.8).

For solids or liquids, which have some compressibility but a small coefficient of thermal expansion, the heat capacities are approximately equal, as shown by the following example.

Example: liquid water at 20°C and 10 MPa

The pertinent properties are: $\alpha = 2.0 \times 10^{-4} \text{ K}^{-1}$; $\beta = 4.4 \times 10^{-4} \text{ MPa}^{-1}$; $v = 1.04 \times 10^{-3} \text{ m}^3/\text{kg}$
With these values, Eq (7.25) gives:

$$C_p - C_v = 0.5 \text{ J/mole-K} = 0.06R$$

By way of comparison, C_p of water is 75 J/mole-K or 9.0R. The difference in the heat capacities of this substance is clearly negligible.

Equations (7.23b) and (7.24b) provide the starting points for calculating the effect of specific volume on C_v and of pressure on C_p . Because, as a thermodynamic property, ds must be an exact differential, Eq (7.4) applies to the coefficients of dT and dv in Eq (7.23b). The terms in Eq (7.1) can be paired with the corresponding terms in Eq (7.23b) by: $x = T$, $y = p$, $M = C_v/T$, $N = (\partial p/\partial T)_v$. Using these identifications in Eq (7.4) yields:

$$\left(\frac{\mathcal{J}C_v}{\mathcal{J}v} \right)_T = T \left(\frac{\mathcal{J}^2 p}{\mathcal{J}T^2} \right)_v = T \frac{\mathcal{J}}{\mathcal{J}T} \left(\frac{\mathbf{a}}{\mathbf{b}} \right)_v \quad (7.26)$$

The second equality utilizes Eq (7.8).

Analogous identification of the coefficients of dT and dp in Eq (7.24b) with M and N in Eq (7.4) yields:

$$\left(\frac{\mathcal{J}C_p}{\mathcal{J}p} \right)_T = -T \left(\frac{\mathcal{J}^2 v}{\mathcal{J}T^2} \right)_p = -T \frac{\mathcal{J}}{\mathcal{J}T} (\mathbf{a}v)_p \quad (7.27)$$

For ideal gases, the second derivatives in Eqs (7.26) and (7.27) are zero, and the heat capacities are independent of pressure or specific volume. The second equalities in Eqs (7.26) and (7.27) employ the definitions of α and β given by Eq (1.2). These forms are useful for applications to condensed phases. The effect of p and v on C_p and C_v is small compared to the influence of temperature.

Example: What change in C_p is caused by increasing the pressure of liquid water at 20°C by 10 MPa?

Assuming α to be constant over the pressure range considered, Eq (7.27) simplifies to:

$$\left(\frac{\partial C_p}{\partial p} \right)_T \cong -\alpha^2 T v = -(2 \times 10^{-4})^2 (293)(1.04 \times 10^{-3}) = -1.2 \times 10^{-8} \frac{\text{J / mole} - \text{K}}{\text{N / m}^2}$$

For a pressure increase of 10 MPa (10^7 n/m^2), C_p decreases from 75 to 74.9 J/mole-K.

Example: Application to a nonideal gas

This example demonstrates the method of integrating the differentials represented by Eqs (7.21) - (7.24) between two states of different temperature and pressure. The gas (N_2) obeys the Van der Waals equation of state in order to highlight the importance of the nonideality corrections if the pressures are sufficiently high.

The path of the process is 1A2 shown in Fig. 7.2. The enthalpy difference $h_2 - h_1$ is to be calculated from the two-step process: an isobaric step from 1 to A followed by an isothermal step from A to 2.

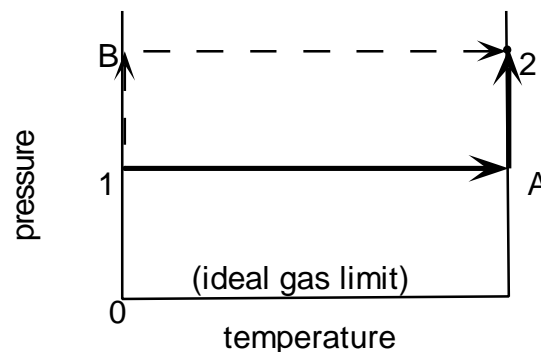


Fig. 7.2 Two paths of a system from state 1 to state 2

The equation of state of the gas is given by Eq (2.4):

$$v = \frac{RT}{p} + b - \frac{a}{RT} \quad (7.28)$$

where $a = 0.14 \text{ J} \cdot \text{m}^3 / \text{mole}^2$ and $b = 3.9 \times 10^{-5} \text{ m}^3 / \text{mole}$. The conditions at states 1 and 2 are: $T_1 = 200 \text{ K}$, $p_1 = 0.1 \text{ MPa}$ and $T_2 = 300 \text{ K}$, $p_2 = 10 \text{ MPa}$.

Level 0 in Fig. 7.2 represents the ideal gas limit, where the heat capacity is $C_{p0} = 29.1$ J/mole-K. From this value, the heat capacity at pressure p_1 is calculated by substituting Eq (7.28) into Eq (7.27) and integrating from $p_0 \sim 0$ to p_1 :

$$C_{p1} = C_{p0} + \frac{2ap_1}{RT^2} \quad (7.29)$$

This result is used to determine the enthalpy change for the temperature increase from state 1 to intermediate state A:

$$h_A - h_1 = \int_{T_1}^{T_2} C_{p1} dT = C_{p0}(T_2 - T_1) + \frac{2ap_1}{RT_1} \left(1 - \frac{T_1}{T_2}\right) = 2910 + 6 = 2916 \quad \frac{J}{mole}$$

The pressure correction to C_{p0} amounts to less than 0.2% of the first term that utilizes the ideal gas heat capacity.

For the isothermal step from state A to the final state 2, the second term in Eq (7.22b) is integrated using v given by Eq (7.28):

$$h_2 - h_A = \int_{p_1}^{p_2} \left[v - T \left(\frac{\partial v}{\partial T} \right)_p \right] dp = - \left(\frac{2a}{RT_2} - b \right) (p_2 - p_1) = -736 \quad \frac{J}{mole}$$

For this step, the pressure nonideality correction is $\sim 25\%$ of the ideal gas Δh . The total enthalpy change,

$$h_2 - h_1 = 2916 - 736 = 2180 \text{ J/mole}$$

is significantly smaller than the ideal gas value of 2910 J/mole.

The choice of the path 1A2 to perform the calculation is purely a matter of calculational convenience. Any other path from state 1 to state 2, such as 1B2 in Fig. 7.2, would produce the same value of $h_2 - h_1$.

7.4 Relations for nonideal gases with special process restraints

The analyses in Sect. 7.3 treated the effects of changes in p , T , and v on the dependent-variable properties u , h , and s . The partial derivatives that appear in these relations (Eqs(7.21)-(7.24)) involved only the EOS variables p , T , and v . In the present section, the roles of the independent and dependent variables are reversed. We analyze processes in which s , u , and h are held constant and determine the behavior of the p - v - T variables. In all cases, the system is a nonideal gas.

Isentropic process

Isentropic expansion of an ideal gas was treated in Sect. 3.7. Here, the same process is analyzed without the restriction of ideality. Equation (7.23b) is divided by dv while holding s constant, which produces the relation:

$$\left(\frac{\mathcal{H}}{\mathcal{V}}\right)_s = -\frac{T}{C_V} \left(\frac{\mathcal{H}p}{\mathcal{H}T}\right)_v \quad (7.30)$$

To illustrate the effect of gas nonideality on property changes during an isentropic expansion, the right hand side of Eq (7.30) is evaluated for a Van der Waals gas obeying the equation of state given by Eq (2.5):

$$p = \frac{RT}{v-b} - \frac{a}{v^2} \quad (7.31)$$

Substituting Eq (7.31) into Eq (7.30) yields:

$$\left(\frac{\mathcal{H}}{\mathcal{V}}\right)_s = -\frac{RT}{C_V(v-b)}$$

In the limit of low pressure, the specific heats are independent of p (or v) and their difference is the gas constant. The nonideal gas effect on C_V is given by Eq (7.26). For the Van der Waals gas described by Eq (7.31), $(\mathcal{H}^2 p / \mathcal{H}T^2)_v = 0$, so C_V is not a function of v. Substituting $R = C_{P0} - C_{V0}$, setting $C_V = C_{V0}$ and using the symbol γ for C_{P0}/C_{V0} , the above equation becomes:

$$\left(\frac{\mathcal{H}}{\mathcal{V}}\right)_s = -(\gamma - 1) \frac{T}{(v-b)}$$

Integrating between states 1 and 2 gives:

$$T_2 = T_1 \left(\frac{v_1 - b}{v_2 - b}\right)^{\gamma-1} \quad (7.32)$$

If the gas were ideal, the parameter b would vanish from Eq (7.32), and Eq (3.17) would be recovered.

Example: If N_2 ($\gamma = 1.4$) is compressed isentropically from atmospheric pressure and 20°C to 10 MPa, find the final temperature if (a) ideality is assumed and (b) nonideality is characterized by the Van der Waals parameters given in connection with Eq (7.28).

In state 1, N_2 is very nearly ideal, so $v_1 = 2.44 \times 10^{-2} \text{ m}^3/\text{mole}$. However, v_2 cannot be immediately calculated because it depends on T_2 , which is also an unknown. To overcome this difficulty, Eq (7.31) is written for the conditions of state 2, solved for T_2 and equated to the right hand side of Eq (7.32). The result is:

$$\frac{T_2}{T_1} = \frac{v_2 - b}{RT_1} \left(p_2 - \frac{a}{v_2^2}\right) = \left(\frac{v_1 - b}{v_2 - b}\right)^{\gamma-1}$$

Solving the second equality numerically yields $v_2 = 9.4 \times 10^{-4} \text{ m}^3/\text{mole}$ and the first equality gives $T_2 = 1098 \text{ K}$. If the gas were assumed to behave ideally, the simpler formulas of Eqs (3.16) and (3.17) would yield $(v_2)_{\text{id}} = 9.1 \times 10^{-4} \text{ m}^3/\text{mole}$ and $(T_2)_{\text{id}} = 1092 \text{ K}$. For the process conditions used in this example, the nonideality corrections are modest.

Problems 7.5 and 7.6 provide additional exercises involving isentropic processes of nonideal gases.

Joule Expansion (constant internal energy process)

One of the simplest yet most significant experiments in the long history of thermodynamics was performed in 1843 by James Joule. The experimental setup consisted of two vessels connected by a valve and immersed in a water bath with a thermometer to detect any temperature changes arising from cooling or heating effects in the two vessels. Initially, one vessel contained air at 2 MPa and the other was evacuated. When the valve connecting them was opened and the gas expanded to fill both vessels equally, no increase in the temperature of the water bath was noted. Since the system consisting of the water bath and the pair of vessels is one of constant internal energy, Joule concluded that the internal energy of the air does not depend on its specific volume. This key feature of ideal gases was stated without proof in Sect. 2.4.

Joule's experiment can be modified to more clearly reveal the thermal effects of expansion of a nonideal gas when its internal energy is held constant. Or, how is the partial derivative $(\partial T/\partial v)_u$ related to the equation of state of the gas? The modification of the Joule experiment consists of eliminating the water bath, insulating the two vessels against heat flow from outside, and placing the thermometer directly in the first vessel. For simplicity, the valve is replaced by a membrane that is ruptured to initiate gas expansion. The apparatus is shown in Fig. 7.3.

To relate the temperature difference between the two states shown in Fig. 7.3 to the equation of state, Eq(7.21b) is divided by dv with u held constant. This yields the desired coefficient:

$$\left(\frac{\mathcal{T}}{\mathcal{V}}\right)_u = \frac{1}{C_v} \left[p - T \left(\frac{\mathcal{P}}{\mathcal{T}}\right)_v \right] \quad (7.33)$$

For an ideal gas, it is readily seen that the right hand side of this equation is zero, which is the theoretical basis for Joule's observation of the lack of temperature change on expansion in his experiment. Thus, Joule's experiment proved that the heat capacity of ideal gases depend only on temperature.

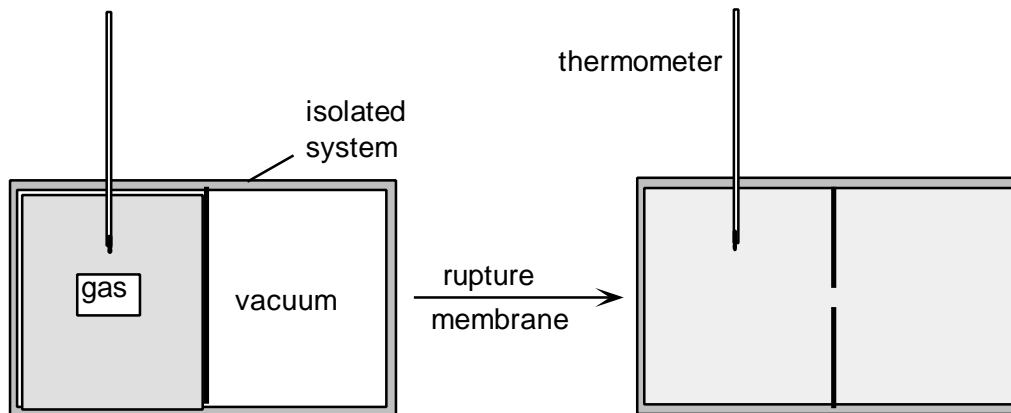


Fig. 7.3 Modified Joule apparatus to measure the temperature change on expansion of a nonideal gas at constant internal energy.

If an equation of state appropriate to a nonideal gas is used in the bracketed term in Eq (7.33), the temperature change on expansion can be predicted. If the initial pressure is sufficiently high and the initial temperature low enough, the nonideal effect will be large enough to be measured in the experiment shown in Fig. 7.3.

Example: What is the change in temperature of nitrogen when the specific volume initially at 20°C and 10 MPa is doubled at constant internal energy?

Noting that $C_v = C_{v0} = 7/2R = 29.1$ J/mole-K, and using Eq (7.31) for the equation of state in Eq (7.33) yields:

$$\left(\frac{\partial T}{\partial v} \right)_u = -\frac{a}{C_{v0}v^2}$$

Integrating from v_1 to $2v_1$ gives a temperature change of:

$$\Delta T = -\frac{a}{2C_{v0}v_1} = -\frac{ap_1}{2C_{v0}RT_1} = -\frac{(0.14)(10^7)}{(2)(29.1)(8.314)(293)} = -10^\circ C$$

It is clear from this equation that measurement of the gas temperature decrease in a Joule expansion provides a means of experimentally determining the coefficient a in the Van der Waals equation under conditions in which the gas exhibits nonideal behavior.

The Joule-Thompson Coefficient (constant enthalpy process)

In Sect. 4.4, it was shown that flow of a fluid through a device that exchanges neither heat nor work with the surroundings and involves negligible kinetic energy changes proceeds without change in enthalpy (see Eq (4.7)). Valves, porous plugs, and orifices

inserted into flow lines are examples of devices through which the flow is isenthalpic. Even though the enthalpies upstream and downstream of such devices are equal, the pressures are not. In fact, the main practical purpose of these devices is to produce an abrupt reduction in pressure, and for refrigerators, of temperature as well. For this reason, they are called throttling devices.

If the fluid is a gas, the change in temperature across the device may be positive, negative, or zero, depending on the equation of state and the upstream temperature. The partial derivative $(\partial T/\partial p)_h$ representing this process is called the *Joule-Thompson coefficient*. If the gas is ideal, no change in temperature occurs because the enthalpy is constant. Some gases with positive Joule-Thompson coefficients are useful as refrigerants.

The relation between the Joule-Thompson coefficient and the equation of state is obtained from Eq (7.22b) by dividing by dp while holding h constant:

$$\left(\frac{\partial T}{\partial p}\right)_h = \frac{1}{C_p} \left[T \left(\frac{\partial v}{\partial T}\right)_p - v \right] \quad (7.34)$$

This equation is the enthalpy analog of Eq (7.33). It is obtained from the latter by exchanging p for v and h for u .

Example: If N_2 at 20°C is reduced in pressure in a throttling device from 10 MPa to 0.1 MPa, what is the temperature change?

According to Eq (7.27), C_p of a nonideal gas depends on pressure. However, this effect is of second order, and it suffices to approximate C_p by the ideal gas value: $C_p = C_{p0} = 9/2R = 37.4$ J/mole-K. Substituting the Van der Waals EOS, Eq (7.28), into Eq (7.34) and using the constants for N_2 yields:

$$\left(\frac{\partial T}{\partial p}\right)_h = \frac{1}{C_p} \left[\frac{2a}{RT} - b \right] = 2 \times 10^{-6} \frac{K}{Pa} = 2 \frac{K}{MPa}$$

The 9.9 MPa pressure drop over the throttling device is accompanied by a 20°C temperature decrease.