

GENERAL THERMODYNAMIC RELATIONSHIPS: FOR SINGLE COMPONENT SYSTEMS OR SYSTEMS OF CONSTANT COMPOSITION

The relationships which follow are based on single component systems or systems of constant composition. These are a subset of the more general equations which can be derived, and which allow for changes in composition. It will be shown in Chapter 12 that if a change in composition occurs then another term called chemical potential, μ , which defines the effect of this change is required.

7.1 THE MAXWELL RELATIONSHIPS

The concept of functional relationships between properties was introduced previously. For example, the Second Law states that, for a reversible process, T , s , u , p and v are related in the following manner.

$$TdS = dU + pdV \quad (7.1)$$

or, in specific (or molar) terms

$$Tds = du + pdv \quad (7.1a)$$

Rearranging Eqn (7.1a) enables the change of internal energy, du , to be written as

$$du = Tds - pdv \quad (7.2)$$

i.e.

$$u = f(s, v) \quad (7.2a)$$

It will be shown that in Chapter 12, in the general case where the composition can change, Eqn (7.1) should be written as

$$TdS = du + pdV - \sum_i \mu_i dn_i \quad (7.1b)$$

where,

μ_i = chemical potential of component i and

n_i = amount of component i .

The chemical potential terms will be omitted in the following analysis, although similar equations to those below can be derived by taking them into account.

It can be seen from Eqns (7.2) and (7.2a) that the specific internal energy can be represented by a three-dimensional surface based on the independent variables of entropy and specific volume. If this surface is *continuous* then the following relationships can be derived based on the mathematical properties of the surface. The restriction of a continuous surface means that it is 'smooth'. It can be seen from Fig. 2.5 that the p - v - T surface for water is continuous over most of the surface, but there are discontinuities at the saturated liquid and saturated vapour lines shown in Fig. 2.6. Hence, the following relationships apply over the major regions of the surface, *but not across the boundaries*. For a continuous surface,

$$z = z(x, y) \quad \text{where } z \text{ is a continuous function.}$$

Then,

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

Let

$$M = \left(\frac{\partial z}{\partial x} \right)_y \quad \text{and} \quad N = \left(\frac{\partial z}{\partial y} \right)_x. \quad (7.4)$$

Then,

$$dz = Mdx + Ndy. \quad (7.5)$$

For continuous functions the derivatives $\frac{\partial^2 z}{\partial x \partial y}$ and $\frac{\partial^2 z}{\partial y \partial x}$ are equal, and hence $\left(\frac{\partial M}{\partial y} \right)_x = \left(\frac{\partial N}{\partial x} \right)_y$. Consider also the expressions obtained when $z = z(x, y)$ and x and y are themselves related to additional variables u and v , such that $x = x(u, v)$ and $y = y(u, v)$. Then,

$$\left(\frac{\partial z}{\partial u} \right)_v = \left(\frac{\partial z}{\partial x} \right)_y \left(\frac{\partial x}{\partial u} \right)_v + \left(\frac{\partial z}{\partial y} \right)_x \left(\frac{\partial y}{\partial u} \right)_v \quad (7.6)$$

Let $z = v$ and $u = x$, then $x = x(z)$ and

$$\left(\frac{\partial z}{\partial u} \right)_v = 0, \quad \text{and} \quad \left(\frac{\partial x}{\partial u} \right)_v = 1. \quad (7.7)$$

Hence

$$0 = \left(\frac{\partial z}{\partial x} \right)_y + \left(\frac{\partial z}{\partial y} \right)_x \left(\frac{\partial y}{\partial x} \right)_z \quad (7.8)$$

giving

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

These expressions will now be used to consider relationships derived previously. The following functional relationships have already been obtained.

$$du = Tds - pdv \quad (7.10)$$

$$dh = Tds + vdp \quad (7.11)$$

$$df = -pdv - sdT \quad (7.12)$$

$$dg = vdp - sdT \quad (7.13)$$

Consider the expression for du , given in Eqn (7.10) then, by analogy with Eqn (7.3),

$$T = \left(\frac{\partial u}{\partial s} \right)_v, -p = \left(\frac{\partial u}{\partial v} \right)_s \quad \text{and} \quad \left(\frac{\partial T}{\partial v} \right)_s = - \left(\frac{\partial p}{\partial s} \right)_v \quad (7.14)$$

In a similar manner the following relationships can be obtained, *for constant composition or single component systems*:

$$T = \left(\frac{\partial h}{\partial s} \right)_p, v = \left(\frac{\partial h}{\partial p} \right)_s; \left(\frac{\partial T}{\partial p} \right)_s = \left(\frac{\partial v}{\partial s} \right)_p \quad (7.15)$$

$$-p = \left(\frac{\partial f}{\partial v} \right)_T, -s = \left(\frac{\partial f}{\partial T} \right)_v; \left(\frac{\partial p}{\partial T} \right)_v = \left(\frac{\partial s}{\partial v} \right)_T \quad (7.16)$$

$$v = \left(\frac{\partial g}{\partial p} \right)_T, -s = \left(\frac{\partial g}{\partial T} \right)_p, \left(\frac{\partial v}{\partial T} \right)_p = - \left(\frac{\partial s}{\partial p} \right)_T. \quad (7.17)$$

If the pairs of relationships for T are equated then,

$$\left(\frac{\partial u}{\partial s} \right)_v = \left(\frac{\partial h}{\partial s} \right)_p \quad (7.18a)$$

and, similarly

$$\left(\frac{\partial g}{\partial p} \right)_T = \left(\frac{\partial h}{\partial p} \right)_s \quad (7.18b)$$

$$\left(\frac{\partial u}{\partial v} \right)_s = \left(\frac{\partial f}{\partial v} \right)_T \quad (7.18c)$$

$$\left(\frac{\partial g}{\partial T} \right)_p = \left(\frac{\partial f}{\partial T} \right)_v \quad (7.18d)$$

In addition to these equivalences, Eqns (7.14)–(7.17) also show that

$$\left(\frac{\partial T}{\partial v} \right)_s = - \left(\frac{\partial p}{\partial s} \right)_v \quad (7.19a)$$

$$\left(\frac{\partial T}{\partial p} \right)_s = \left(\frac{\partial v}{\partial s} \right)_p \quad (7.19b)$$

$$\left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T \quad (7.19c)$$

$$\left(\frac{\partial v}{\partial T}\right)_p = -\left(\frac{\partial s}{\partial p}\right)_T \quad (7.19d)$$

Equations (7.19) are called the *Maxwell relationships*.

7.1.1 GRAPHICAL INTERPRETATION OF MAXWELL RELATIONS

Let a system comprising a pure substance execute a small reversible cycle 1-2-3-4-1 consisting of two isochors separated by dV and two isentropes separated by ds ; these cycles are shown in Fig. 7.1 (a) and (b).

If the cycles are reversible the area on the T - s diagram must equal the area on the p - v diagram. Now the difference in pressure between lines 1 and 2 is given by $\left(\frac{\partial p}{\partial s}\right)_v ds$, and to the first order the difference in pressure between lines 3 and 4 is the same. Hence, the area on the p - v diagram is

$$\left(\frac{\partial p}{\partial s}\right)_v ds dv. \quad (7.20a)$$

Applying the same approach to the T - s diagram, the difference in temperature between lines 1 and 4 is $-\left(\frac{\partial T}{\partial v}\right)_s dv$, which is negative because the temperature decreases as the volume increases, and the area of the diagram is

$$-\left(\frac{\partial T}{\partial v}\right)_s dv ds. \quad (7.20b)$$

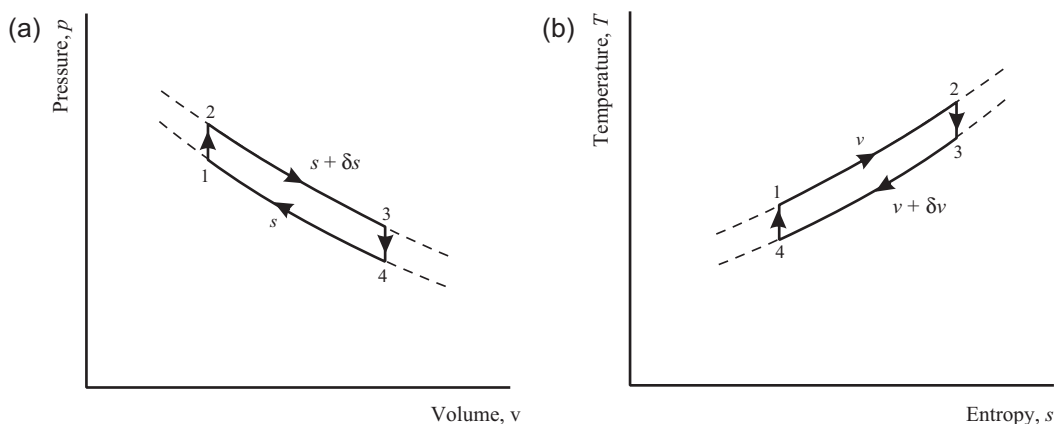


FIGURE 7.1

Elemental cycles illustrating the Maxwell relationships. (a) Pressure-volume diagram, (b) temperature-entropy diagram.

Thus, equating the two areas gives

$$-\left(\frac{\partial T}{\partial v}\right)_s dv ds = \left(\frac{\partial p}{\partial s}\right)_v ds dv. \quad (7.21)$$

and hence

$$\left(\frac{\partial p}{\partial s}\right)_v = -\left(\frac{\partial T}{\partial v}\right)_s. \quad (7.19a)$$

7.2 USES OF THE THERMODYNAMIC RELATIONSHIPS

When performing certain types of calculation it is useful to have data on the values of the specific heat capacities of the substance under consideration and also the variation of these specific heat capacities with the other properties. The specific heat capacities themselves are first derivatives of the internal energy (u) and the enthalpy (h), and hence the variations of specific heat capacities are second derivatives of the basic properties.

By definition, the specific heat capacity at constant volume is

$$c_v = \left(\frac{\partial u}{\partial T}\right)_v = \left(\frac{\partial u}{\partial s}\right)_v \left(\frac{\partial s}{\partial T}\right)_v. \quad (7.22)$$

But

$$\left(\frac{\partial u}{\partial s}\right)_v = T, \text{ and thus } c_v = T \left(\frac{\partial s}{\partial T}\right)_v. \quad (7.23)$$

Similarly

$$c_p = \left(\frac{\partial h}{\partial T}\right)_p = \left(\frac{\partial h}{\partial s}\right)_p \left(\frac{\partial s}{\partial T}\right)_p = T \left(\frac{\partial s}{\partial T}\right)_p. \quad (7.24)$$

Consider the variation of the specific heat capacity at constant volume, c_v , with specific volume, v , if the temperature is maintained constant. This can be derived in the following way.

$$\left(\frac{\partial c_v}{\partial v}\right)_T = \frac{\partial}{\partial v} \left[T \left(\frac{\partial s}{\partial T}\right)_v \right] = T \frac{\partial^2 s}{\partial v \partial T} = T \frac{\partial}{\partial T} \left(\frac{\partial s}{\partial v}\right)_T.$$

Now, from Eqn (7.19c),

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

giving

$$\left(\frac{\partial c_v}{\partial v}\right)_T = T \left(\frac{\partial^2 s}{\partial T \partial v}\right) = T \left(\frac{\partial^2 p}{\partial T^2}\right)_v \quad (7.25)$$

7.2.1 SPECIFIC HEAT AT CONSTANT VOLUME, c_v , AS A FUNCTION OF VOLUME

Hence, if data are available for a substance in the form of a p - v - T surface (e.g. Fig. 2.5), or a mathematical relationship, it is possible to evaluate $(\partial^2 p / \partial T^2)_v$ and then $(\partial c_v / \partial v)_T$. By integration, it is then possible to obtain the values of c_v at different volumes. For example, consider whether the specific heat capacity at constant volume is a function of the volume of both an ideal gas and a van der Waals gas.

Ideal gas

The gas relationship for an ideal gas is

$$pv = RT \quad (7.26)$$

and

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{v}; \text{ and } \left(\frac{\partial^2 p}{\partial T^2}\right)_v = 0. \quad (7.27)$$

Hence

$$c_v \neq f(v)$$

for an ideal gas.

This is in agreement with Joule's experiment for assessing the change of internal energy, u , with volume.

van der Waals gas

The van der Waals gas is discussed in much greater depth in Section 8.2; the equation of state will just be introduced here and some of the concepts developed above will be investigated.

The equation of state of a van der Waals gas is

$$p = \frac{RT}{v - b} - \frac{a}{v^2}, \quad (7.28)$$

where a and b are constants (described in Section 8.2).

Hence

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{v - b}; \text{ and } \left(\frac{\partial^2 p}{\partial T^2}\right)_v = 0. \quad (7.29)$$

Again,

$$c_v \neq f(v)$$

for a van der Waals gas.

So, for 'gases' obeying these state equations $c_v \neq f(v)$, but in certain cases and under certain conditions c_v could be a function of the volume of the system and it would be calculated in this way. Of course, if these equations are to be integrated to evaluate the internal energy it is necessary to know the value of c_v at a datum volume and temperature.

7.2.2 SPECIFIC HEAT AT CONSTANT PRESSURE, c_p , AS A FUNCTION OF PRESSURE

Similarly, the variation of the specific heat capacity at constant pressure with pressure can be investigated by differentiating the specific heat capacity with respect to pressure, giving

$$\left(\frac{\partial c_p}{\partial p}\right)_T = \frac{\partial}{\partial p} \left(T \left(\frac{\partial s}{\partial T} \right)_p \right)_T = T \frac{\partial}{\partial T} \left(\frac{\partial s}{\partial p} \right)_T = -T \left(\frac{\partial^2 v}{\partial T^2} \right)_p \quad (7.30)$$

This equation can be used to see if the specific heat capacity at constant pressure of gases obeying the ideal gas law and those obeying van der Waals equation are functions of pressure. This is done below.

Ideal gas

$$pv = RT \quad (7.26)$$

Hence

$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{R}{p}; \quad \text{and} \quad \left(\frac{\partial^2 v}{\partial T^2}\right)_p = 0. \quad (7.31)$$

This means that the specific heat capacity at constant pressure for a gas obeying the ideal gas law is not a function of pressure, i.e. $c_p \neq f(p)$ for an ideal gas. This conclusion is in agreement with the Joule–Thomson experiment for superheated gases.

van der Waals gas

$$p = \frac{RT}{v-b} - \frac{a}{v^2}. \quad (7.28)$$

Equation (7.28) can be rewritten as

$$\left(p + \frac{a}{v^2}\right)(v-b) = RT,$$

which expands to

$$pv + \frac{a}{v} - pb - \frac{ab}{v^2} = RT.$$

Differentiating implicitly gives

$$p \left(\frac{\partial v}{\partial T} \right)_p + (-) \frac{a}{v^2} \left(\frac{\partial v}{\partial T} \right)_p - \frac{(-2)ab}{v^3} \left(\frac{\partial v}{\partial T} \right)_p = R,$$

which can be rearranged to give

$$\left(\frac{\partial v}{\partial T} \right)_p \left\{ p - \frac{a}{v^2} + \frac{2ab}{v^3} \right\} = R,$$

and hence

$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{R}{p - \frac{a}{v^2} \left(1 - \frac{2b}{v}\right)} \quad (7.33)$$

This can be differentiated again to give

$$\left(\frac{\partial^2 v}{\partial T^2}\right)_p = \frac{\partial}{\partial T} \left(\frac{\partial v}{\partial T}\right)_p$$

which results in

$$\left(\frac{\partial^2 v}{\partial T^2}\right)_p \left\{p - \frac{a}{v^2} + \frac{2ab}{v^3}\right\} + \left(\frac{\partial v}{\partial T}\right)_p^2 \left\{\frac{2a}{v^3} - \frac{6ab}{v^4}\right\} = 0$$

giving

$$\left(\frac{\partial^2 v}{\partial T^2}\right)_p = \frac{-\left(\frac{\partial v}{\partial T}\right)_p^2 \left\{\frac{2a}{v^3} - \frac{6ab}{v^4}\right\}}{\left\{p - \frac{a}{v^2} + \frac{2ab}{v^3}\right\}}$$

which, on substituting for $\left(\frac{\partial v}{\partial T}\right)_p$ becomes

$$\left(\frac{\partial^2 v}{\partial T^2}\right)_p = -\frac{R^2 \left(\frac{2a}{v^3} - \frac{6ab}{v^4}\right)}{\left(p - \frac{a}{v^2} \left(1 - \frac{2b}{v}\right)\right)^3} \quad (7.34)$$

Hence, for a van der Waals gas, $c_p = f(p)$.

This means that allowance would have to be taken of this when evaluating the change of specific heat capacity at constant pressure for a process in which the pressure is changed. This can be evaluated from

$$c_p = \int_{p_1}^{p_2} -T \left(\frac{\partial^2 v}{\partial T^2}\right)_p dp, \quad (7.35)$$

where $\left(\frac{\partial^2 v}{\partial T^2}\right)_p$ is calculated from Eqn (7.34).

7.3 Tds RELATIONSHIPS

Two approaches have been used previously in performing cycle calculations. When evaluating the performance of steam plant and refrigeration equipment, much emphasis was placed on the use of tables and if the work done between two states was required, enthalpy values at these states were evaluated and suitable subtractions were performed. When doing cycle calculations for gas turbines and internal combustion engines, the air was assumed to be an ideal gas and the specific heat capacity

was used. The most accurate way of performing such calculations is, in fact, to use the enthalpy or internal energy values because these implicitly integrate the specific heat capacity over the range involved. The following analyses will demonstrate how these values of internal energy and enthalpy are obtained.

The two-property rule can be used to define entropy as the following functional relationship.

$$s = s(v, T) \quad (7.36)$$

Hence

$$ds = \left(\frac{\partial s}{\partial T} \right)_v dT + \left(\frac{\partial s}{\partial v} \right)_T dv. \quad (7.37)$$

Now, by definition

$$c_v = T \left(\frac{\partial s}{\partial T} \right)_v$$

and from the Maxwell relationships, Eqn (7.19c), $\left(\frac{\partial s}{\partial v} \right)_T = \left(\frac{\partial p}{\partial T} \right)_v$

Hence

$$Tds = c_v dT + T \left(\frac{\partial p}{\partial T} \right)_v dv \quad (7.38)$$

This is called the *first Tds relationship*

The second Tds relationship can be derived in the following way. If it is assumed that entropy, s , is a function of temperature and pressure alone, then

$$s = s(T, p). \quad (7.39)$$

and

$$ds = \left(\frac{\partial s}{\partial T} \right)_p dT + \left(\frac{\partial s}{\partial p} \right)_T dp. \quad (7.40)$$

By definition,

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

and, from Eqn (7.19d)

$$\left(\frac{\partial s}{\partial p} \right)_T = - \left(\frac{\partial v}{\partial T} \right)_p.$$

Thus, the *second Tds relationship* is

$$Tds = c_p dT - T \left(\frac{\partial v}{\partial T} \right)_p dp. \quad (7.41)$$

The *third Tds relationship* is derived by assuming that

$$s = s(p, v). \quad (7.42)$$

$$ds = \left(\frac{\partial s}{\partial p} \right)_v dp + \left(\frac{\partial s}{\partial v} \right)_p dv. \quad (7.43)$$

Now, by definition,

$$c_p = T \left(\frac{\partial s}{\partial T} \right)_p = T \left(\frac{\partial s}{\partial v} \right)_p \left(\frac{\partial v}{\partial T} \right)_p,$$

giving

$$\left(\frac{\partial s}{\partial v} \right)_p = \frac{1}{T} c_p \left(\frac{\partial T}{\partial v} \right)_p.$$

A similar expression can be derived for c_v , and this enables the equation

$$Tds = c_v \left(\frac{\partial T}{\partial p} \right)_v dp + c_p \left(\frac{\partial T}{\partial v} \right)_p dv \quad (7.44)$$

to be obtained. This is the *third Tds relationship*.

7.3.1 VARIATION OF INTERNAL ENERGY AND ENTHALPY

It is now possible to investigate the variation of internal energy and enthalpy with independent properties for gases obeying various gas laws.

The internal energy of a substance can be expressed as

$$u = u(T, v). \quad (7.45)$$

Hence, the change in internal energy is

$$du = \left(\frac{\partial u}{\partial T} \right)_v dT + \left(\frac{\partial u}{\partial v} \right)_T dv \quad (7.46)$$

Now

$$c_v = \left(\frac{\partial u}{\partial T} \right)_v$$

and from the Second Law,

$$du = Tds - pdv. \quad (7.47)$$

Substituting for Tds in [Eqn \(7.47\)](#) from first Tds relation ([Eqn \(7.38\)](#)) gives,

$$du = c_v dT + T \left(\frac{\partial p}{\partial T} \right)_v dv - pdv \quad (7.48)$$

and hence Eqn (7.46) becomes

$$c_v dT + T \left(\frac{\partial p}{\partial T} \right)_v dv - p dv = c_v dT + \left(\frac{\partial u}{\partial v} \right)_T dv. \quad (7.49)$$

or

$$\left(\frac{\partial u}{\partial v} \right)_T = \left[T \left(\frac{\partial p}{\partial T} \right)_v - p \right] \quad (7.50)$$

Equation (7.50) can be used to evaluate the variation in internal energy with volume for both ideal and van der Waals gases.

Ideal gas

The equation of state of an ideal gas is $p v = R T$ and hence

$$\left(\frac{\partial p}{\partial T} \right)_v = \frac{R}{v} \quad (7.51)$$

Thus

$$\left(\frac{\partial u}{\partial v} \right)_T = \left[\frac{R T}{v} - p \right] = 0. \quad (7.52)$$

Hence, the specific internal energy of an ideal gas is not a function of its specific volume (or density). This is in agreement with Joule's experiment that $u \neq f(v)$ at constant temperature.

van der Waals gas

The equation of state of a van der Waals gas is

$$p = \frac{R T}{v - b} - \frac{a}{v^2},$$

and hence

$$\left(\frac{\partial p}{\partial T} \right)_v = \frac{R}{v - b} \quad (7.53)$$

which gives the change of internal energy with volume as

$$\left(\frac{\partial u}{\partial v} \right)_T = \left[\frac{R T}{v - b} - p \right] = \frac{a}{v^2}. \quad (7.54)$$

This means that the internal energy of a van der Waals gas is a function of its specific volume or density. This is not surprising because density is a measure of the closeness of the molecules of the substance (see Section 8.2), and the internal energy variation is related to the force of attraction between the molecules. This means that some of the internal energy in a van der Waals gas is stored in the attraction forces between the molecules, and not all of the thermal energy is due to molecular motion, as was the case for the ideal gas.

Now, if it is required to calculate the total change in internal energy, u , for a change in volume and temperature, it is necessary to use Eqn (7.46)

$$du = \left(\frac{\partial u}{\partial T} \right)_v dT + \left(\frac{\partial u}{\partial v} \right)_T dv. \quad (7.46)$$

For an *ideal gas*

$$du = \left(\frac{\partial u}{\partial T} \right)_v dT = c_v dT. \quad (7.55)$$

i.e. for an ideal gas

$$u = f(T).$$

It is also possible to use the following approach to show whether $u = f(p)$. This may be done in the following way.

$$\left(\frac{\partial u}{\partial v} \right)_T = \left(\frac{\partial u}{\partial p} \right)_T \left(\frac{\partial p}{\partial v} \right)_T = 0.$$

Now

$$\left(\frac{\partial p}{\partial v} \right)_T = -\frac{p}{v},$$

and since

$$p \neq 0, \left(\frac{\partial u}{\partial p} \right)_T = 0.$$

Hence, for an ideal gas

$$u \neq f(p).$$

For a *van der Waals gas*

$$du = c_v dT + \frac{a}{v^2} dv. \quad (7.56)$$

Hence, for a van der Waals gas $u = f(T, v)$.

7.4 RELATIONSHIPS BETWEEN SPECIFIC HEAT CAPACITIES

These relationships enable the value of one specific heat capacity to be calculated if the other is known. This is useful because it is much easier to measure the specific heat capacity at constant pressure, c_p , than that at constant volume, c_v .

Using the two-property rule it is possible to write

$$s = s(T, v) \quad (7.57)$$

and, if s is a continuous function of temperature and volume

$$ds = \left(\frac{\partial s}{\partial T} \right)_v dT + \left(\frac{\partial s}{\partial v} \right)_T dv. \quad (7.58)$$

If Eqn (7.58) is differentiated with respect to temperature, T , with p maintained constant, then

$$\left(\frac{\partial s}{\partial T} \right)_p = \left(\frac{\partial s}{\partial T} \right)_v + \left(\frac{\partial s}{\partial v} \right)_T \left(\frac{\partial v}{\partial T} \right)_p. \quad (7.59)$$

The definitions of the specific heat capacities are $c_v = T \left(\frac{\partial s}{\partial T} \right)_v$ and $c_p = T \left(\frac{\partial s}{\partial T} \right)_p$.
Hence

$$\frac{c_p - c_v}{T} = \left(\frac{\partial s}{\partial v} \right)_T \left(\frac{\partial v}{\partial T} \right)_p. \quad (7.60)$$

From Maxwell relations,

$$\left(\frac{\partial s}{\partial v} \right)_T = \left(\frac{\partial p}{\partial T} \right)_v \quad (7.19c)$$

Thus

$$\frac{c_p - c_v}{T} = \left(\frac{\partial p}{\partial T} \right)_v \left(\frac{\partial v}{\partial T} \right)_p. \quad (7.61)$$

The mathematical relationship in Eqn (7.9)

$$\left(\frac{\partial p}{\partial T} \right)_v \left(\frac{\partial T}{\partial v} \right)_p \left(\frac{\partial v}{\partial p} \right)_T = -1 \quad (7.62)$$

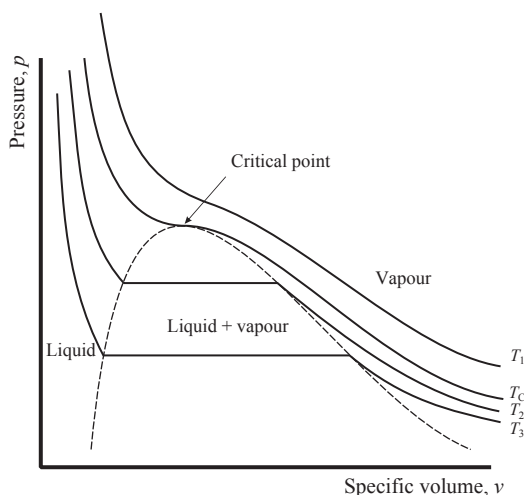
can be rearranged to give

$$\left(\frac{\partial p}{\partial T} \right)_v = - \left(\frac{\partial p}{\partial v} \right)_T \left(\frac{\partial v}{\partial T} \right)_p \quad (7.63)$$

Thus

$$c_p - c_v = -T \left(\frac{\partial p}{\partial v} \right)_T \left(\frac{\partial v}{\partial T} \right)_p^2 \quad (7.64)$$

Examination of Eqn (7.64) can be used to define which specific heat capacity is the larger. First, it should be noted that T and $\left(\frac{\partial v}{\partial T} \right)_p^2$ are both positive, and hence the sign of $c_p - c_v$ is controlled by the sign of $\left(\frac{\partial p}{\partial v} \right)_T$. Now, for all known substances, $(\partial p / \partial v)_T$ is negative. If it were not negative then the substance would be completely unstable because a positive value means that as the pressure is increased the volume increases, and vice versa. Hence, if the pressure on such a substance were decreased its volume would decrease until it ceased to exist.

**FIGURE 7.2**

p - v section of a state diagram showing isotherms.

Thus, $c_p - c_v$ must always be positive or zero, i.e. $c_p \geq c_v$. The circumstances when $c_p = c_v$ are when $T = 0$ or when $(\partial p / \partial T)_v = 0$, e.g. at 4 °C for water (see the p - v - T surfaces in Fig. 2.5). It can also be shown that $c_p \geq c_v$ by considering the terms in Eqn (7.61) in relation to the state diagrams for substances, as shown in Fig. 7.2. The term $(\partial p / \partial T)_v$ that can be evaluated along a line at constant volume, v , can be seen to be positive, because as the temperature increases the pressure increases over the whole of the section. Similarly, $(\partial v / \partial T)_p$, which can be evaluated along a line at constant pressure, p , is also positive. If both these terms are positive then $c_p \geq c_v$.

Now, consider $c_p - c_v$ for an ideal gas that is depicted by the superheated region in Fig. 7.2. The state equation for an ideal gas is

$$pv = RT \quad (7.26)$$

Differentiating gives

$$\left(\frac{\partial p}{\partial v} \right)_T = -\frac{p}{v} \quad (7.65)$$

and

$$\left(\frac{\partial v}{\partial T} \right)_p = \frac{R}{p} \quad (7.66)$$

Thus

$$c_p - c_v = -T \left(\frac{-p}{v} \right) \frac{R^2}{p^2} = R. \quad (7.67)$$

The definition of an ideal gas is one which obeys the ideal gas equation (Eqn (7.26)), and in which the specific heat capacity at constant volume (or pressure) is a function of temperature alone,

i.e. $c_v = f(T)$. Hence, from Eqn (7.67), $c_p = c_v + R = f(T) + R = f'(T)$ if R is a function of T alone. Hence, the difference of specific heat capacities for an ideal gas is the gas constant, R .

Also

$$\left(\frac{\partial p}{\partial v}\right)_T = -\frac{1}{kv} \text{ and } \left(\frac{\partial v}{\partial T}\right)_p = \beta v.$$

Thus

$$c_p - c_v = -T \left(\frac{-1}{kv}\right) (\beta v)^2 = \frac{T\beta^2 v}{k}, \quad (7.68)$$

where

β = coefficient of expansion (isobaric expansivity) and
 k = isothermal compressibility.

Expressions for the difference between the specific heat capacities, $c_p - c_v$, have been derived above. It is also interesting to examine the ratio of specific heat capacities, $\kappa = c_p/c_v$.

The definitions of c_p and c_v are $c_v = T \left(\frac{\partial s}{\partial T}\right)_v$ and $c_p = T \left(\frac{\partial s}{\partial T}\right)_p$, and thus the ratio of specific heat capacities is

$$\frac{c_p}{c_v} = \frac{(\partial s/\partial T)_p}{(\partial s/\partial T)_v}. \quad (7.69)$$

Now, from the mathematical relationship (Eqn (7.9)) for the differentials,

$$\left(\frac{\partial s}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_s \left(\frac{\partial p}{\partial s}\right)_T = -1 = \left(\frac{\partial s}{\partial T}\right)_v \left(\frac{\partial T}{\partial v}\right)_s \left(\frac{\partial v}{\partial s}\right)_T \quad (7.70)$$

giving

$$\frac{c_p}{c_v} = \left(\frac{\partial T}{\partial v}\right)_s \left(\frac{\partial v}{\partial s}\right)_T \left(\frac{\partial p}{\partial T}\right)_s \left(\frac{\partial s}{\partial p}\right)_T \quad (7.71)$$

From the Maxwell relationships

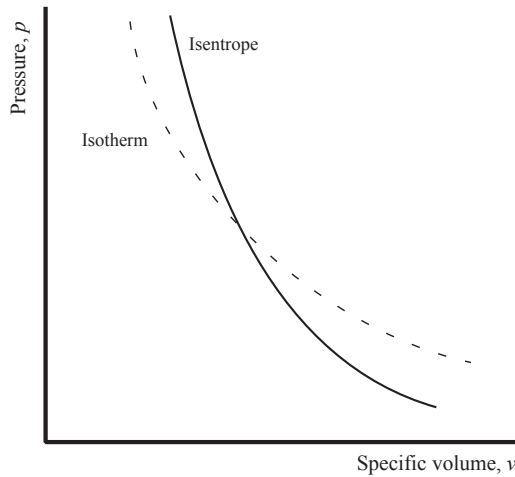
$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v, \quad (7.19c)$$

and

$$\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p \quad (7.19d)$$

giving

$$\begin{aligned} \frac{c_p}{c_v} &= -\left(\frac{\partial T}{\partial v}\right)_s \left(\frac{\partial T}{\partial p}\right)_v \left(\frac{\partial p}{\partial T}\right)_s \left(\frac{\partial v}{\partial T}\right)_p \\ &= -\left(\frac{\partial p}{\partial v}\right)_s \left(\frac{\partial T}{\partial p}\right)_v \left(\frac{\partial v}{\partial T}\right)_p \end{aligned} \quad (7.72)$$

**FIGURE 7.3**

Isentropic and isothermal lines for a perfect gas.

Now, from the two-property rule, $T = T(p, v)$ and hence

$$\left(\frac{\partial p}{\partial v}\right)_T = -\left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial T}{\partial v}\right)_p \quad (7.73)$$

Thus

$$\frac{c_p}{c_v} = \left(\frac{\partial p}{\partial v}\right)_s \bigg/ \left(\frac{\partial p}{\partial v}\right)_T = v \left(\frac{\partial p}{\partial v}\right)_s \bigg/ v \left(\frac{\partial p}{\partial v}\right)_T \quad (7.74)$$

The denominator of Eqn (7.74), $v(\partial p/\partial v)_T$, is the reciprocal of the *isothermal compressibility*, k . By analogy, the numerator can be written as $1/k_s$, where k_s = *adiabatic, or isentropic, compressibility*.

Thus

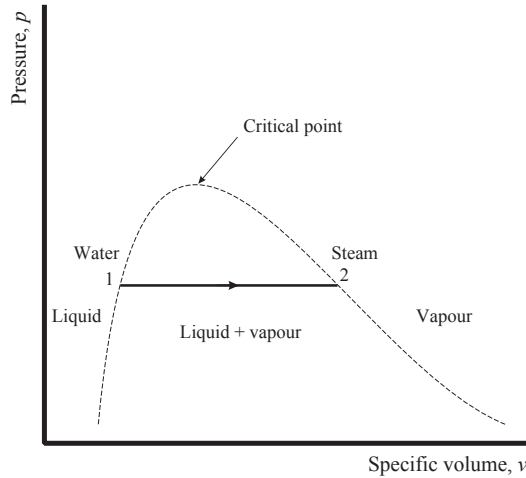
$$\frac{c_p}{c_v} = \frac{k}{k_s} = \kappa. \quad (7.75)$$

If the slopes of isentropes in the p - v plane, are compared with the slopes of isotherms, see Fig. 7.3, it can be seen that $c_p/c_v > 1$ for a gas in the superheat region.

7.5 THE CLAUSIUS-CLAPEYRON EQUATION

From the Maxwell relationships

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v. \quad (7.19c)$$

**FIGURE 7.4**

Change of phase depicted on p – v diagram.

The left hand side of Eqn (7.19c) is the rate of change of entropy with volume at constant temperature.

If the change of phase of water, from, say, liquid to steam is considered, then this takes place at constant pressure and constant temperature, known as *the saturation values*. Hence, if the change of phase between points 1 and 2 on Fig. 7.4 is considered

$$\left(\frac{\partial s}{\partial v}\right)_T = \frac{s_2 - s_1}{v_2 - v_1}, \quad (7.76)$$

which, on substituting from Eqn (7.19c) becomes

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{s_2 - s_1}{v_2 - v_1} \quad (7.77)$$

If there is a mixture of two phases, say steam and water, then the pressure is a function of temperature alone, as shown in Section 8.4. Thus

$$\frac{dp}{dT} = \frac{s_2 - s_1}{v_2 - v_1}. \quad (7.78)$$

Now $\left(\frac{\partial h}{\partial s}\right)_p = T$, and during a change of phase both T and p are constant, giving $h_2 - h_1 = T(s_2 - s_1)$.

Thus

$$\frac{h_2 - h_1}{v_2 - v_1} = T \frac{dp}{dT} \quad (7.79)$$

This equation is known as the *Clapeyron equation*. Now, $h_2 - h_1$ is the latent heat, h_{fg} . If point 1 is on the saturated liquid line and point 2 is on the saturated vapour line, then Eqn (7.79) can be rewritten as

$$T \frac{dp}{dT} = \frac{h_{fg}}{v_{fg}}. \quad (7.80)$$

This can be depicted graphically, and is shown on Fig. 7.5.

If the processes shown on Figs 7.5(a) and (b) are reversible, then the areas are equivalent to the work done. If the two diagrams depict the same processes on different state diagrams then the areas of the ‘cycles’ must be equal. Hence

$$(v_2 - v_1)dp = (s_2 - s_1)dT \quad (7.81)$$

Now, the change of entropy is

$$s_{fg} = s_2 - s_1 = \frac{h_{fg}}{T}, \quad \text{giving} \quad T \frac{dp}{dT} = \frac{h_{fg}}{v_{fg}} \quad (7.82)$$

The graphical approach has confirmed the *Clausius–Clapeyron equation*.

7.5.1 THE USE OF THE CLAUSIUS–CLAPEYRON EQUATION

If an empirical expression is known for the saturation pressure and temperature, then it is possible to calculate the change of entropy and specific volume due to the change in phase. For example, the change of enthalpy and entropy during the evaporation of water at 120 °C can be evaluated from the slope of the saturation line defined as a function of pressure and temperature. The values of entropy and enthalpy for dry saturated steam can also be evaluated if their values in the liquid state are known. An extract of the properties of water is given in Table 7.1, and values of pressure and temperature on the saturation line have been taken at adjacent temperatures.

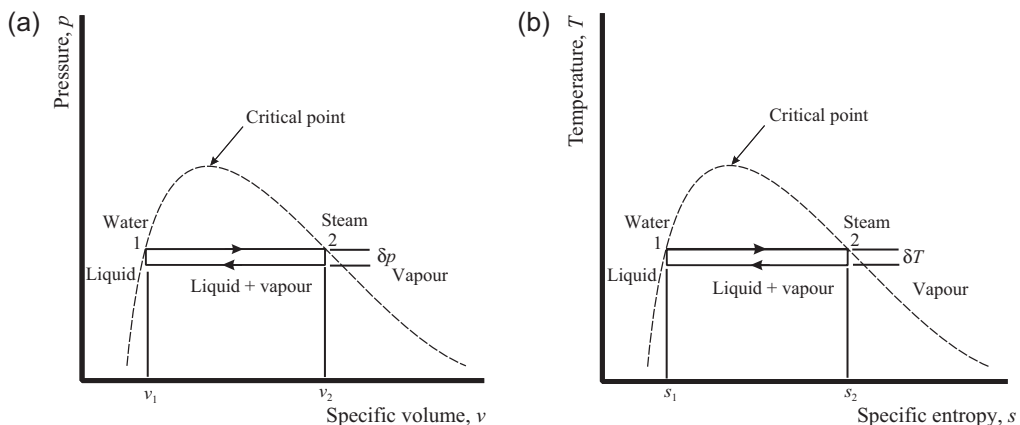


FIGURE 7.5

Evaporation processes shown on state diagrams. (a) p – v diagram; (b) T – s diagram.

Table 7.1 Excerpt from Steam Tables, Showing Values on the Saturated Liquid and Vapour Lines (Rogers and Mayhew (1994)).

Temperature (°C)	Pressure (bar)	Specific Volume (m ³ /kg)	Change of Specific Volume, v_{fg}	Entropy of Liquid, s_f (kJ/kg K)	Enthalpy of Liquid, h_f (kJ/kg K)
115	1.691				
120	1.985	0.001060	0.8845	1.530	505
125	2.321				

At 120 °C, the slope of the saturation line is $\frac{dp}{dT} \approx \frac{2.321 - 1.691}{10} \times 10^5 = 6.30 \times 10^3$.

From the Clausius–Clapeyron equation, Eqn (7.82)

$$\frac{s_2 - s_1}{v_{fg}} = \frac{dp}{dT} = \frac{s_g - s_f}{v_{fg}},$$

giving

$$\begin{aligned} s_g &= s_f + v_{fg} \frac{dp}{dT} = 1.530 + 0.8845 \times 6.30 \times 10^3 / 10^3 \\ &= 1.530 + 5.57235 = 7.102 \text{ kJ/kg K} \end{aligned}$$

The specific enthalpy on the saturated vapour line is

$$\begin{aligned} h_g &= h_f + T s_{fg} \\ &= 505 + (120 + 273) \times 5.57235 \\ &= 2694.9 \text{ kJ/kg K} \end{aligned}$$

These values are in good agreement with the tables of properties; the value of $s_g = 7.127$ kJ/kg K, while $h_g = 2707$ kJ/kg at a temperature of 120.2 °C.

7.6 CONCLUDING REMARKS

Thermodynamic relationships between properties have been developed which are independent of a particular fluid. These can be used to evaluate derived properties from primitive ones and to extend empirical data.

7.7 PROBLEMS

P7.1 For a van der Waals gas that obeys the state equation

$$p = \frac{RT}{v - b} - \frac{a}{v^2}$$

shows that the coefficient of thermal expansion, β , is given by

$$\beta = \frac{Rv^2(v-b)}{RTv^3 - 2a(v-b)^2}$$

and the isothermal compressibility, k , is given by

$$k = \frac{v^2(v-b)^2}{RTv^3 - 2a(v-b)^2}$$

Also evaluate $T\left(\frac{\partial p}{\partial v}\right)_T\left(\frac{\partial v}{\partial T}\right)_p^2$ for the van der Waals gas. From this find $c_p - c_v$ for an ideal gas,

stating any assumptions made in arriving at the solution.

P7.2 Prove the general thermodynamic relationship

$$\left(\frac{\partial c_p}{\partial p}\right)_T = -T\left(\frac{\partial^2 v}{\partial T^2}\right)_p$$

and evaluate an expression for the variation of c_p with pressure for a van der Waals gas which obeys a law

$$p = \frac{\Re T}{v_m - b} - \frac{a}{v_m^2},$$

where the suffix, m , indicates molar quantities and \Re is the Universal gas constant.

It is possible to represent the properties of water by such an equation, where

$$a = 5.525 \frac{(\text{m}^3)^2 \text{ bar}}{(\text{kmol})^2}; \quad b = 0.03042 \frac{\text{m}^3}{\text{kmol}}; \quad \Re = 8.3143 \text{ kJ/kmol K}.$$

Evaluate the change in c_p as the pressure of superheated water vapour is increased from 175 bar to 200 bar at a constant temperature of 425 °C. Compare this with the value you would expect from the steam tables abstracted below.

t (°C)	$p = 175 \text{ bar}$		$p = 200 \text{ bar}$	
	v (m ³ /kg)	h (kJ/kg)	v (m ³ /kg)	h (kJ/kg)
425	0.013914	3014.9	0.011458	2952.9
450	0.015174	3109.7	0.012695	3060.1

What is the value of $\left(\frac{\partial c_p}{\partial p}\right)_T$ of a gas which obeys the Clausius equation of state, $p = \frac{\Re T}{v_m - b}$?

P7.3 Show that if the ratio of the specific heats is 1.4, then

$$\left(\frac{\partial p}{\partial T}\right)_s = \frac{7}{2} \left(\frac{\partial p}{\partial T}\right)_v.$$

P7.4 Show that

$$(a) \quad h - u = T^2 \left(\left(\frac{\partial(f/T)}{\partial T} \right)_v - \left(\frac{\partial(g/T)}{\partial T} \right)_p \right)$$

$$(b) \quad \frac{c_p}{c_v} = \left(\frac{\partial^2 g}{\partial T^2} \right)_p \bigg/ \left(\frac{\partial^2 f}{\partial T^2} \right)_v.$$

P7.5 Show

$$(a) \quad T ds = c_p dT - T \left(\frac{\partial v}{\partial T} \right)_p dp$$

$$(b) \quad T ds = c_v \left(\frac{\partial T}{\partial p} \right)_v dp + c_p \left(\frac{\partial T}{\partial v} \right)_p dv$$

$$(c) \quad \left(\frac{\partial h}{\partial p} \right)_T = v - T \left(\frac{\partial v}{\partial T} \right)_p.$$

P7.6 Show that, for a pure substance,

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

and from this, prove that

$$c_p - c_v = T \left(\frac{\partial p}{\partial T} \right)_v \left(\frac{\partial v}{\partial T} \right)_p.$$

The following table gives values of the specific volume of water, in cubic metres per kilogram. A quantity of water is initially at 30 °C, 20 bar and occupies a volume of 0.2 m³. It is heated at constant volume to 50 °C and then cooled at constant pressure to 30 °C. Calculate the net heat transfer to the water.

Pressure (bar)	Specific Volume (m ³ /kg)	
	20	200
Temperature (°C)		
30	0.0010034	0.0009956
50	0.0010112	0.0010034

[438 kJ]

P7.7 Assuming that entropy is a continuous function, $s = s(T, v)$, derive the expression for entropy change

$$ds = c_v \frac{dT}{T} + \left(\frac{\partial p}{\partial T} \right)_v dv$$

and similarly, for $s = s(T, p)$ derive

$$ds = c_p \frac{dT}{T} - \left(\frac{\partial v}{\partial T} \right)_p dp.$$

Apply these relationships to a gas obeying van der Waals equation

$$p = \frac{RT}{v - b} - \frac{a}{v^2}$$

and derive an equation for the change of entropy during a process in terms of the basic properties and gas parameters. Also derive an expression for the change of internal energy as such a gas undergoes a process.

$$\left[s_2 - s_1 = c_p \ln \frac{T_2}{T_1} - R \ln \left(\frac{p_2 + a/v_2^2 - 2a(v-b)/v_2^3}{p_1 + a/v_1^2 - 2a(v-b)/v_1^3} \right); u_2 - u_1 = \int_1^2 c_v dT - a \left(\frac{v_1 - v_2}{v_1 v_2} \right) \right]$$