

CHAPTER 4: *Classic Thermodynamics*
 Part III: More About Thermal Parameters

4.1 Introduction

Thermodynamic processes, by design or by nature, can take place under conditions in which specific macroscopic parameters -- e. g. temperature, pressure, volume, magnetic field, entropy -- remain constant. Descriptions of such processes can often be made more practical by defining auxiliary thermal parameters that incorporate these conditions.

4.2 The Thermodynamic Identity*

The thermodynamic identity is written

$$dS = \frac{1}{T} dU + \frac{p}{T} dV \quad (4.1)$$

This functional dependence $S = S(U, V)$ expresses entropy in terms of its *natural* variables. The total differential dS is, alternatively,

$$dS = \left(\frac{\partial S}{\partial U} \right)_V dU + \left(\frac{\partial S}{\partial V} \right)_U dV \quad (4.2)$$

which when compared with Eq. (4.1) gives the thermodynamic identities

$$\left(\frac{\partial S}{\partial U} \right)_V = \frac{1}{T} \quad (4.3)$$

$$\left(\frac{\partial S}{\partial V} \right)_U = \frac{p}{T} \quad (4.4)$$

Furthermore, applying Euler's condition gives

$$\left[\frac{\partial}{\partial V} \left(\frac{1}{T} \right) \right]_U = \left[\frac{\partial}{\partial U} \left(\frac{p}{T} \right) \right]_V \quad (4.5)$$

which is evaluated as

*. In magnetic or elastic systems other reversible "work" terms make an appearance in which case correspondence between p and V with other thermodynamic variables are readily made.

$$\left(\frac{\partial T}{\partial V}\right)_U = p\left(\frac{\partial T}{\partial U}\right)_V - T\left(\frac{\partial p}{\partial U}\right)_V \quad (4.6)$$

Groups of relations such as Eqs. (4.3) - (4.6) are valuable for calculating changes in thermodynamic systems due to changes in governing parameters.

Sometimes trivial rearrangements can give other useful expressions. For example, rearranging the thermodynamic identity [see Eq. (4.1)] as

$$dU = TdS - pdV \quad (4.7)$$

suggests a functional relation $U = U(S, V)$ with the total differential

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV \quad (4.8)$$

Comparing this with Eq. (4.7) gives the connection identities

$$\left(\frac{\partial U}{\partial S}\right)_V = T \quad (4.9)$$

$$\left(\frac{\partial U}{\partial V}\right)_S = -p \quad (4.10)$$

to which Euler's condition adds

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V \quad (4.11)$$

Expressions like Eqs. (4.6) and (4.11) are, as a class, called Maxwell relations.

4.3 Helmholtz Free Energy

The Helmholtz free energy F is defined as the combination of state variables

$$F = U - TS \quad (4.12)$$

An interpretation of this quantity can be had by first taking the total differential

$$dF = dU - TdS - SdT. \quad (4.13)$$

Substituting for dU from Eq. (4.7), we find

$$dF = -SdT - pdV \quad (4.14)$$

The Helmholtz free energy remains constant ($dF = 0$) at constant temperature, constant volume processes. At constant temperature Eq. (4.14) becomes

$$-dF = pdV \quad (4.15)$$

where pdV is typical of reversible infinitesimal work. Since reversible work is the maximum work that can be done by a system, the decrease in Helmholtz free energy is equal to the maximum work a system can perform at constant temperature.

According to Eq. (4.14) F is naturally expressed as $F = F(T, V)$ so that we have the total differential

$$dF = \left(\frac{\partial F}{\partial T}\right)_V dT + \left(\frac{\partial F}{\partial V}\right)_T dV \quad (4.16)$$

Comparing this with Eq. (4.14) we find the pair of thermodynamic identities

$$\left(\frac{\partial F}{\partial T}\right)_V = -S \quad (4.17)$$

and

$$\left(\frac{\partial F}{\partial V}\right)_T = -p \quad (4.18)$$

Moreover, since F is an exact function, the Euler criterion gives

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V, \quad (4.19)$$

another of the legendary *Maxwell relations*.

4.4 Enthalpy

The Enthalpy H is defined by

$$H = U + pV \quad (4.20)$$

with the total differential dH

$$dH = dU + pdV + Vdp \quad (4.21)$$

Substituting Eq. (4.7) for dU we have

$$dH = TdS - Vdp. \quad (4.22)$$

Enthalpy is a state variable that remains constant in isentropic, constant pressure processes. These are the conditions that characterize thermodynamic "throttling" which is used in the process of refrigeration.

At constant pressure enthalpy is the reversible heat entering or leaving a system.

H is naturally expressed as $H = H(S, p)$ with the differential

$$dH = \left(\frac{\partial H}{\partial S}\right)_p dS + \left(\frac{\partial H}{\partial p}\right)_S dp \quad (4.23)$$

Comparing this with Eq. (10.22) we find the thermodynamic identities

$$\left(\frac{\partial H}{\partial S}\right)_p = T \quad (4.24)$$

and

$$\left(\frac{\partial H}{\partial p}\right)_S = -V \quad (4.25)$$

Since H is exact, Euler's condition gives

$$\left(\frac{\partial T}{\partial p}\right)_S = -\left(\frac{\partial V}{\partial S}\right)_p \quad (4.26)$$

which is another Maxwell relation.

4.5 Gibbs Free Energy

A Gibbs free energy G is defined as

$$G = U - TS + pV \quad (4.27)$$

with the total differential

$$dG = dU - TdS - SdT + pdV + Vdp \quad (4.28)$$

Substituting for dU in the thermodynamic identity we have

$$dG = -SdT + Vdp \quad (4.29)$$

The Gibbs free energy remains constant in processes taking place at constant temperature and pressure which are experimental constraints for most chemical reactions and some phase transitions. It is *natural* to write $G = G(T, p)$ so that the differential dG is

$$dG = \left(\frac{\partial G}{\partial T} \right)_p dT + \left(\frac{\partial G}{\partial p} \right)_T dp \quad (4.30)$$

Comparing this with Eq. (4.29) we have the thermodynamic identities

$$\left(\frac{\partial G}{\partial T} \right)_p = -S \quad (4.31)$$

$$\left(\frac{\partial G}{\partial p} \right)_T = V \quad (4.32)$$

Applying Euler's condition gives yet another Maxwell relation

$$\left(\frac{\partial S}{\partial p} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_p \quad (4.33)$$

4.6 Applying Thermodynamic Relations

(1) Consider a total derivative

$$dU = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV \quad (4.34)$$

which might be required in finding the change in internal energy of a system under changes in temperature and volume. The first partial derivative is just the constant volume heat capacity

$$\left(\frac{\partial U}{\partial T} \right)_V = C_V \quad (4.35)$$

But the second partial derivative in Eq. (4.34) is not obviously related to system properties, i.e.

such as appear in an equation of state. However if we start with

$$F = U - TS \quad (4.36)$$

and take the *constant temperature* partial derivatives with respect to volume we have

$$\left(\frac{\partial F}{\partial V}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T - T\left(\frac{\partial S}{\partial V}\right)_T \quad (4.37)$$

Then using Eq. (4.18) we arrive at a somewhat improved situation

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p. \quad (4.38)$$

Substituting the Maxwell relation of Eq. (4.19) finally transforms Eq. (4.37) into the more transparent result

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p \quad (4.39)$$

which was found in Chapter 3 by a somewhat longer route. Therefore Eq. (4.34) is equivalent to

$$dU = C_v dT + \left[T\left(\frac{\partial p}{\partial T}\right)_V - p \right] dV \quad (4.40)$$

(2) The Joule-Thompson coefficient discussed in Chapter 3 is

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H \quad (4.41)$$

A first step in its practical evaluation is to apply the cyclic chain rule

$$\begin{aligned} \left(\frac{\partial T}{\partial P}\right)_H &= -\frac{\left(\frac{\partial H}{\partial p}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_p} \\ &= -\frac{1}{C_p} \left(\frac{\partial H}{\partial p}\right)_T \end{aligned} \quad (4.42)$$

Now, with the Gibbs free energy

$$G = H - TS \quad (4.43)$$

we take the constant temperature derivative

$$\left(\frac{\partial G}{\partial p}\right)_T = \left(\frac{\partial H}{\partial p}\right)_T - T\left(\frac{\partial S}{\partial p}\right)_T \quad (4.44)$$

But from Eqs. (4.31) and (4.32) we have

$$\left(\frac{\partial G}{\partial p}\right)_T = V \quad (4.45)$$

and the Maxwell relation

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \quad (4.46)$$

Therefore

$$V = \left(\frac{\partial H}{\partial p}\right)_T + T\left(\frac{\partial V}{\partial T}\right)_p \quad (4.47)$$

and finally Eq. (4.41) becomes

$$z = \frac{1}{C_p} \left[T \left(\frac{\partial V}{\partial T}\right)_p - V \right] \quad (4.48)$$

For an ideal gas $z = 0$. But a real gas with intermolecular forces -- such as a van der Waals gas

$$\left(p + \frac{a}{v^2}\right)(v - b) = k_B T \quad (4.49)$$

where v is the volume per molecule -- behaves quite differently.

As discussed in Chapter 3, if $z < 0$ a gas will cool when throttled whereas if $z > 0$ the gas will warm. This has enormous practical consequences for design of commercial and scientific (ultra low temperature) refrigerators. The curve $z(p, T) = 0$ defines the *boundary* between the two regions and is called the *inversion curve*.

4.7 Heat Capacity and Entropy

Heat capacities describe the relationship between infinitesimal temperature changes that take place as a consequence of infinitesimal heat reversibly entering or leaving a system. Further narrowing the definition, a list of state variables that are held constant during the reversible process is included. We define then a *heat capacity* at constant α , where α is a list of thermodynamic variables held constant in the process, as

$$\delta Q_{rev} = C_{\alpha} dT \quad (\text{constant } \alpha) \quad (4.50)$$

In many experimental situations the variable held constant is volume or pressure. This is particularly practical in the case of gases. The heat capacity at constant volume is then written as

$$\delta Q_{rev} = C_V dT \quad (\text{constant } V) \quad (4.51)$$

The heat capacity at constant pressure is

$$\delta Q_{rev} = C_p dT \quad (\text{constant } p) \quad (4.52)$$

In solids it is less practical to hold volume constant and measurements are usually made at constant pressure.

For systems whose primary macroscopic parameter is elongation, such as elastic materials, we might be interested in heat capacities at constant length

$$\delta Q_{rev} = C_L dT \quad (\text{constant } L) \quad (4.53)$$

or heat capacities at constant tension

$$\delta Q_{rev} = C_{\tau} dT \quad (\text{constant } \tau) \quad (4.54)$$

Heat capacity measurements are capable of revealing much about the microscopic basis of macroscopic behavior and are high on the list of important thermodynamic experiments. Heat capacity measurements in solids at very low temperature first revealed to Einstein that nature was not as classical as was generally believed at the time. He applied quantization ideas proposed by Planck (1900) to develop the first quantum theory of solids 25 years before the debut of Schrödinger mechanics.

For a reversible process $dS = \delta Q_{rev} / T$, so that heat capacities can always be written

$$C_{\alpha} = T \left(\frac{\partial S}{\partial T} \right)_{\alpha} \quad (4.55)$$

The appearance of entropy in thermodynamics brings a much welcome uniformity to heat capacity definitions. Whereas in Chapter 2 we derived the result

$$C_v = \left(\frac{\partial U}{\partial T} \right)_v, \quad (4.56)$$

by the simple chain rule

$$\left(\frac{\partial U}{\partial T} \right)_v = \left(\frac{\partial U}{\partial S} \right)_v \left(\frac{\partial S}{\partial T} \right)_v. \quad (4.57)$$

Now, from Eq. (4.9) we can write Eq. (4.57) as

$$\left(\frac{\partial U}{\partial T} \right)_v = T \left(\frac{\partial S}{\partial T} \right)_v \quad (4.58)$$

confirming the form of Eq. (4.55).

Similarly, for a reversible process at constant pressure we also have from Chapter 2

$$C_p = \left(\frac{\partial H}{\partial T} \right)_p \quad (4.59)$$

But the chain rule gives

$$\left(\frac{\partial H}{\partial T} \right)_p = \left(\frac{\partial H}{\partial S} \right)_p \left(\frac{\partial S}{\partial T} \right)_p \quad (4.60)$$

Therefore, applying Eq. (4.24) this becomes

$$C_p = \left(\frac{\partial H}{\partial T} \right)_p = T \left(\frac{\partial S}{\partial T} \right)_p \quad (4.61)$$

again in the form of Eq. (4.55).

4.8 A Relationship Between C_p and C_v .

The general relationship between the heat capacities C_p and C_v for any gas is easily found by using the definition(s) in Eqs. (4.54) and (4.55) above. In carrying out the steps for a gas we will see how to manipulate the required partial derivatives with the goal of obtaining expressions involving only p , V and T (the variables related by the equation of state.)

Finding the connection between $T(\partial S/\partial T)_p$ and $T(\partial S/\partial T)_v$ puts the problem on one simplifying footing.

Expressing the entropy as $S = S(T, p)$ is, considering our objective, the sensible variables. Other functional starting points are equivalent but this one offers a direct resolution of the problem.

Now we write the total derivative

$$dS = \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp \quad (4.62)$$

which already contains *something* relevant, i.e.

$$dS = \frac{C_p}{T} dT + \left(\frac{\partial S}{\partial p}\right)_T dp \quad (4.63)$$

Since we want to relate this to C_v we need to turn this expression around by substituting the total differential

$$dp = \left(\frac{\partial p}{\partial T}\right)_v dT + \left(\frac{\partial p}{\partial V}\right)_T dV \quad (4.64)$$

which turns Eq. (4.63) into

$$dS = \left[\frac{C_p}{T} + \left(\frac{\partial S}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_v \right] dT + \left(\frac{\partial S}{\partial V}\right)_T dV \quad (4.65)$$

Now we see that the first coefficient is nothing more than

$$\left(\frac{\partial S}{\partial T}\right)_v = \left[\frac{C_p}{T} + \left(\frac{\partial S}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_v \right] \quad (4.66)$$

or, using the definition of Eq. (4.55)

$$\frac{C_v}{T} = \left[\frac{C_p}{T} + \left(\frac{\partial S}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_v \right] \quad (4.67)$$

which is exactly what we want, except that the partial derivative $(\partial S/\partial p)_T$ is not yet digestible in

terms of an equation of state. But invoking the Maxwell relation in Eq. (4.46) this becomes

$$\frac{C_V}{T} = \left[\frac{C_p}{T} - \left(\frac{\partial V}{\partial T} \right)_p \left(\frac{\partial p}{\partial T} \right)_V \right] \quad (4.68)$$

or

$$C_p - C_V = T \left(\frac{\partial V}{\partial T} \right)_p \left(\frac{\partial p}{\partial T} \right)_V \quad (4.69)$$

which is *exactly* what we want.

For an ideal gas we find

$$\left(\frac{\partial V}{\partial T} \right)_p = \frac{Nk_B}{p}; \quad \left(\frac{\partial p}{\partial T} \right)_V = \frac{Nk_B}{V} \quad (4.70)$$

giving the well known result [see e.g. Halliday and Resnik]

$$C_p - C_V = Nk_B. \quad (4.71)$$

Of course, Eq. (4.69) is a general result so we are not limited to an ideal gas. Any equation of state, including the more accurate and interesting van der Waals equation, can be used. Nor is the result even limited to gasses. A similar result will link, for example, C_B and C_M for magnetic systems or C_T and C_L for linear elastic systems, results which will be used in later chapters.