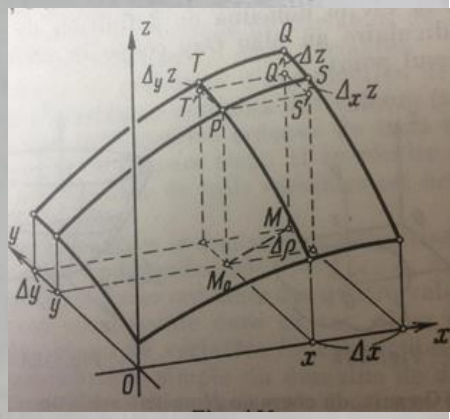
Chapter 2

Heat and Entropy

2.1 The Heat Equations

Thermodynamics becomes a mathematical science when we regard the state functions, such as the internal energy, as continuous differentiable functions of the variables P, V, T. The constraint imposed by the equation of state reduces the number of independent variables to two. We may consider the internal energy to be a function of any two of the variables. Under infinitesimal increments of the variables, we can write



$$dU(P,V) = \left(\frac{\partial U}{\partial P}\right)_V dP + \left(\frac{\partial U}{\partial V}\right)_P dV \tag{1}$$

$$dU(P,T) = \left(\frac{\partial U}{\partial P}\right)_T dP + \left(\frac{\partial U}{\partial T}\right)_P dT \tag{2}$$

$$dU(V,T) = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT \tag{3}$$

where a subscript on a partial derivative denotes the variable being held fixed. For example, $(\partial U/\partial P)_V$ is the derivative with respect to P at constant V. These partial derivatives are thermodynamic coefficients to be taken from experiments.

The heat absorbed by the system can be obtained from the first law, written in the form $dQ = dU + PdV$:

$$dQ = \left(\frac{\partial U}{\partial P}\right)_V dP + \left[\left(\frac{\partial U}{\partial V}\right)_P + P\right] dV \tag{4}$$

$$dQ = \left(\frac{\partial U}{\partial P}\right)_T dP + \left(\frac{\partial U}{\partial T}\right)_P dT + PdV \tag{5}$$

$$dQ = \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] dV + \left(\frac{\partial U}{\partial T}\right)_V dT \tag{6}$$

(2.2)

In the second of these equations we must regard V a function of P, T, and rewrite

$$dV = \left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT \tag{7}$$

(2.3)

The second equation then reads

$$dQ = \left[\left(\frac{\partial U}{\partial P}\right)_T + P\left(\frac{\partial V}{\partial P}\right)_T\right] dP + \left(\frac{\partial (U+PV)}{\partial T}\right)_P dT \tag{2.4}$$

It is convenient to define a state function called the *enthalpy*:

$$H \equiv U + PV \tag{2.5}$$

The heat equations in dQ form are summarized below:

$$dQ = \left(\frac{\partial U}{\partial P}\right)_V dP + \left[\left(\frac{\partial U}{\partial V}\right)_P + P\right] dV$$

$$dQ = \left[\left(\frac{\partial U}{\partial P}\right)_T + P\left(\frac{\partial V}{\partial P}\right)_T\right] dP + \left(\frac{\partial H}{\partial T}\right)_P dT$$

$$dQ = \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] dV + \left(\frac{\partial U}{\partial T}\right)_V dT \tag{2.6}$$

We can immediately read off the heat capacities at constant V and P:

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

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \tag{2.7}$$

These are useful because they express the heat capacities as derivatives of state functions.

2.2 Applications to Ideal Gas

We now use the first law to deduce some properties of the ideal gas. Joule performed a classic experiment on free expansion, as illustrated in Figure 2.1. A thermally insulated ideal gas was allowed to expand freely into an insulated chamber, which was initially vacuous. After a new equilibrium was established, in which the gas fills both compartments, the final temperature was found to be the same as the initial temperature.

We can draw the following conclusions:

- $\Delta W = 0$ (since the gas pushes into a vacuum)
- $\Delta Q = 0$ (since the temperature was unchanged)
- $\Delta U = 0$ (by the first law)

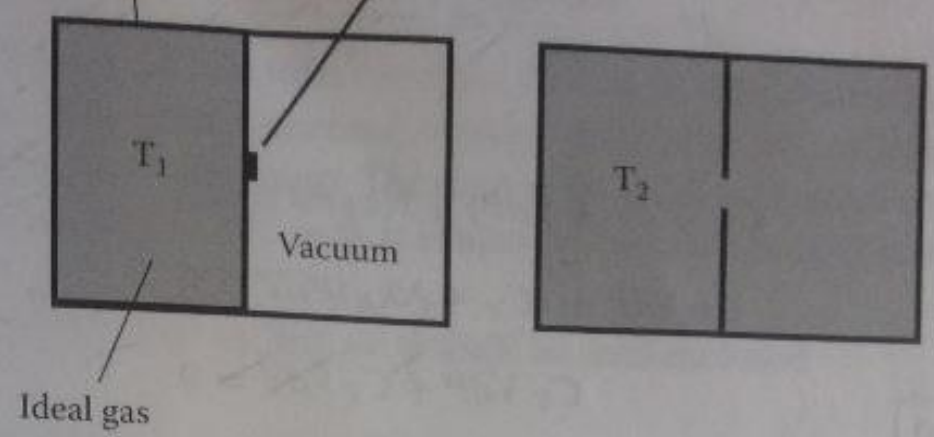


Figure 2.1 Free expansion of an ideal gas.

Choosing V, T as independent variables, we conclude $U(V_1, T) = U(V_2, T)$. That is, U is independent of V:

$$U = U(T) \tag{2.8}$$

Of course, U is proportional to the total number of particle N, which has been kept constant.

The heat capacity at constant volume can now be written as a total derivative:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{dU}{dT} \tag{2.9}$$

Assuming that C_V is a constant, we can integrate the above to obtain

$$U(T) = \int C_V \, dT = C_V T \tag{2.10}$$

where the constant of integration has been set to zero by defining $U = 0$ at $T = 0$. It follows that

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial (U + PV)}{\partial T}\right)_P$$

$$= \frac{dU}{dT} + \frac{\partial (Nk_B T)}{\partial T} \tag{2.11}$$

$$= C_V + Nk_B \tag{2.12}$$

Thus, for an ideal gas,

$$C_P - C_V = Nk_B \tag{2.13}$$

We now work out the equation governing a reversible adiabatic transformation. Setting $dQ = 0$, we have $dU = -PdV$. Since $dU = C_V dT$, we obtain

$$C_V dT + PdV = 0 \tag{2.14}$$

Using the equation of state $PV = Nk_BT$, we can write

$$dT = \frac{d(PV)}{Nk_B} = \frac{PdV + VdP}{Nk_B} \tag{2.15}$$

Thus

$$C_V\,(PdV + VdP) + Nk_BPdV = 0$$

$$C_V\,VdP + (C_V + Nk_B)PdV = 0$$

$$C_V\,VdP + C_PPdV = 0 \tag{2.16}$$

or

$$\frac{dP}{P} + \gamma\frac{dV}{V} = 0 \tag{2.17}$$

where

$$\gamma \equiv \frac{C_P}{C_V} \tag{2.18}$$

Assuming that γ is a constant, we obtain through an integration

$$\ln P = -\gamma\,\ln V + \text{constant} \tag{2.19}$$

or

$$PV^\gamma = \text{constant} \tag{2.20}$$

Using the equation of state, we can rewrite this in the equivalent form

$$TV^{\gamma-1} = \text{constant} \tag{2.21}$$

Since $\gamma > 1$ according to Equation (2.13), an adiabatic path has a steeper slope than an isotherm in a PV diagram, as depicted in Figure 2.2.