

I. FUNDAMENTAL EQUATION FOR THE IDEAL GAS

The equation of state of an ideal gas is,

$$pV = NRT, \quad (1)$$

but we know that one equation of state is not sufficient to specify the fundamental equation of a mono component fluid system. In the case of an ideal gas, it is sufficient to state that the internal energy does not depend on volume (as there is no interatomic potential),

$$\left(\frac{\partial U}{\partial V}\right)_{NT} = 0. \quad (2)$$

In fact we know that $U = cNRT$ with $c = 3/2$ for a mono atomic gas, and $c = 5/2$ for a diatomic molecule.

The fundamental equation can be obtained by integration of the differential form of the Second Law. At constant N we have,

$$TdS = dU + pdV = C_V dT + pdV.$$

By using the equation of state, we have

$$dS = \frac{C_V}{T} dT + \frac{NR}{V} dV$$

which can be integrated between two arbitrary states to yield

$$S(U, N, V) - S_0(U_0, N, V_0) = C_V \ln \frac{T}{T_0} + NR \ln \frac{V}{V_0}, \quad (3)$$

with $T = U/cNR$.

II. EXAMPLE OF THERMODYNAMIC MANIPULATION

Just an example on how to compute the change of a thermodynamic quantity along a particular reversible path. For example, let us compute the change in entropy (**Question:** If we consider a reversible path, why is the change in entropy not zero?).

One can examine S as a function of any arbitrary arguments or variables, up to the number of independent thermodynamic variables for the system at hand. Let us consider a shorter set (take a system and constant N), and let us take as independent variables T and

V , one an intensive parameter, the other an extensive thermodynamic variable. Given our choice, we write $S = S(T, V)$, and hence the differential is,

$$dS = \left(\frac{\partial S}{\partial T} \right)_{NV} dT + \left(\frac{\partial S}{\partial V} \right)_{NT} dV.$$

The next step is to use thermodynamic relations and definitions to compute the partial derivatives appearing in the expression, followed by integration of the differential form.

First we note,

$$T \left(\frac{\partial S}{\partial T} \right)_{NV} = \left(\frac{\partial U}{\partial T} \right)_{NV} = C_V,$$

which gives the first partial derivative. The second can be calculated by using a Maxwell relation $\left(\frac{\partial S}{\partial V} \right)_{NT} = \left(\frac{\partial p}{\partial T} \right)_{VN}$. Using the cyclic identity $\left(\frac{\partial p}{\partial T} \right)_{NV} \left(\frac{\partial V}{\partial p} \right)_{NT} \left(\frac{\partial T}{\partial V} \right)_{Np} = -1$ and the definitions of the two response functions, $\left(\frac{\partial T}{\partial V} \right)_{Np} = 1/\alpha V$ for the coefficient of thermal expansion and $\left(\frac{\partial V}{\partial p} \right)_{NT} = -V\kappa_T$ for the isothermal compressibility, we find

$$dS = \frac{C_V}{T} dT + \frac{\alpha}{\kappa_T} dV. \quad (4)$$

This is the desired result, and holds for any arbitrary mono component fluid system. Equation (4) can now be integrated between any two states provided that three system specific parameters are known as a function of the independent variables. This can be accomplished through experimentation, or theory (e.g., for an ideal gas).

III. ADIABATIC AND REVERSIBLE PROCESS

A particularly interesting process is the adiabatic and reversible process in which the system does not exchange heat with the environment. According to the first law of Thermodynamics, this process is governed by $dQ = dU + pdV = 0$. Let us select as independent variables T and V . We write,

$$dU = \left(\frac{\partial U}{\partial T} \right)_{NV} dT + \left(\frac{\partial U}{\partial V} \right)_{NT} dV.$$

Substituting the adiabatic process condition, we find,

$$C_V(dT)_S + \left[\left(\frac{\partial U}{\partial V} \right)_{NT} + p \right] (dV)_S = 0, \quad (5)$$

where we have added the S subscript to the differentials to indicate that they are not arbitrary variations but along an adiabatic path.

In order to integrate this differential expression, one needs to know C_V , the derivative $(\frac{\partial U}{\partial V})_{NT}$ and the equation of state.

Question: Use this equation to obtain the adiabatic lines of an ideal gas.

A. Alternative calculation

There are many ways -all equivalent- to conduct this calculation. For example, for a reversible adiabatic process, we know that the entropy remains constant. As another example, we could choose as independent variables (N, S, p) , and write $T = T(N, S, p)$. Along a constant entropy path (and constant N), we simply have,

$$dT = \left(\frac{\partial T}{\partial p} \right)_{NS} dp,$$

as the other two differentials are zero for the process chosen. In order to compute the partial derivative we recall that $(\frac{\partial S}{\partial T})_{pN} (\frac{\partial T}{\partial p})_{SN} (\frac{\partial p}{\partial S})_{TN} = -1$, so that

$$\left(\frac{\partial T}{\partial p} \right)_{SN} = - \frac{(\frac{\partial S}{\partial p})_{TN}}{C_p/T},$$

where we have used the definition of the heat capacity at constant pressure. We further use the Maxwell relation $-(\frac{\partial S}{\partial p})_{TN} = (\frac{\partial V}{\partial T})_{pN} = \alpha V$ to arrive at

$$(dT)_{NS} = \frac{\alpha VT}{C_p} dp \tag{6}$$

IV. FREE EXPANSION

This is a frequent but difficult example. A system occupying an initial volume V_i is allowed to rapidly expand to a final volume V_f . Because the process occurs so quickly, it is normally approximated by an adiabatic process as the expanding system hardly has any time to exchange heat with the environment.

The difficulty with the analysis of this process can be illustrated with the case in which the expanding system is an ideal gas. In this case, and by definition, the internal energy does not depend on volume, and hence $dU = 0$. The hypothesis of adiabaticity is $dQ = 0$. However, the fundamental equation for the ideal gas allows one to connect the entropies

of the final and initial states as $S_f - S_i = NR \ln(V_f/V_i) > 0$. Therefore we conclude that $T(S_f - S_i) \neq Q$, the heat exchanged !

The resolution to this apparent discrepancy is that the free expansion is an irreversible process, and that $TdS \neq dQ$. More to the point, the intermediate states are not of equilibrium and hence the variable entropy is simply not defined.

It is certainly possible, instead, to devise a reversible process that connect the same initial and final states (not adiabatic), and to calculate the entropy change along this new process. Since the entropy is a function of state, and if the initial and final states are truly the same for the free expansion as for the reversible process devised, then the entropy change of the reversible process will equal the entropy change of the (irreversible) free expansion.

One possible way is to consider a process at constant internal energy. We have established that the process is very approximately adiabatic, and if we take a free expansion to occur against zero external pressure, then there is no work done by the system. According to the first law, this process would take place at constant internal energy. We write, for example,

$$(dT)_U = \left(\frac{\partial T}{\partial V} \right)_{NU} dV$$

Then $\left(\frac{\partial T}{\partial V} \right)_{NU} \left(\frac{\partial V}{\partial U} \right)_{NT} \left(\frac{\partial U}{\partial T} \right)_{NV} = -1$ yields,

$$\left(\frac{\partial T}{\partial V} \right)_{NU} = - \frac{\left(\frac{\partial U}{\partial V} \right)_{NT}}{C_V}.$$

We now use $dU = TdS - pdV$ along this new process, and by using that $\left(\frac{\partial S}{\partial V} \right) = \left(\frac{\partial p}{\partial T} \right) = \alpha/\kappa_T$ and $\left(\frac{\partial U}{\partial V} \right)_{NT} = T \left(\frac{\partial S}{\partial V} \right)_{NT} - p$, one finds,

$$(dT)_U = \left(\frac{p}{C_V} - \frac{\alpha T}{C_V \kappa_T} \right) dV. \quad (7)$$

Integration of this equation allows the calculation of the temperature change during the free expansion as a function of the increase in volume.

Again, the physical system does not follow a quasi-static path. We would conduct the integration on a thermodynamic path at constant U instead. In this particular case, the path a constant internal energy will (approximately) connect the initial and final states of the free expansion.

Question: Integrate Eq. (7) for an ideal gas.