

## 1 Entropy change in the isobaric-isochoric cycle of an ideal gas

Show that the entropy change in the cyclic process of an ideal gas, that is represented by a rectangle in the  $(P, V)$  diagram, is zero.

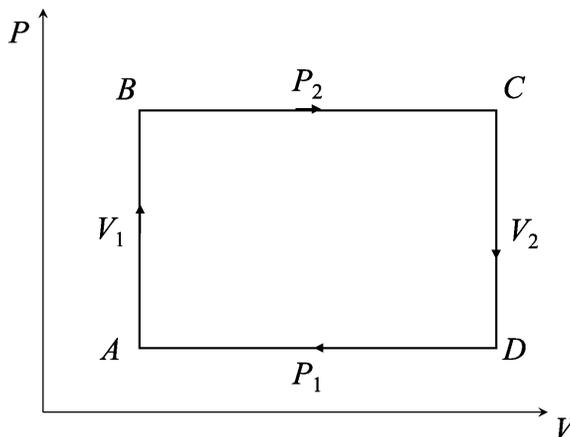


Figure 1: Isobar-isochore cycle.

*Solution:* In the isobaric process of an ideal gas, the infinitesimal amount of heat is given by

$$\delta Q = dU + PdV = C_V dT + PdV.$$

From the equation of state of the ideal gas

$$PV = \nu RT$$

follows

$$T = \frac{PV}{\nu R}, \quad dT = \frac{PdV}{\nu R}$$

Substituting this into

$$dS = \frac{\delta Q}{T},$$

one obtains

$$dS = \frac{C_V PdV/(\nu R) + PdV}{PV/(\nu R)} = (C_V + \nu R) \frac{dV}{V} = C_P \frac{dV}{V}.$$

In the isochoric process of the ideal gas,  $\delta Q$  is given by

$$\delta Q = C_V dT = C_V \frac{VdP}{\nu R},$$

thus

$$dS = \frac{\delta Q}{T} = C_V \frac{VdP}{PV} = C_V \frac{dP}{P}.$$

In our cyclic process,

$$\Delta S_{AB} = \int_{P_1}^{P_2} C_V \frac{dP}{P} = C_V \ln \frac{P_2}{P_1} > 0$$

$$\Delta S_{CD} = C_V \ln \frac{P_1}{P_2} = -\Delta S_{AB}$$

$$\Delta S_{BC} = \int_{V_1}^{V_2} C_P \frac{dV}{V} = C_P \ln \frac{V_2}{V_1} > 0$$

$$\Delta S_{DA} = C_P \ln \frac{V_1}{V_2} = -\Delta S_{BC}.$$

The total entropy change

$$\Delta S = \Delta S_{AB} + \Delta S_{BC} + \Delta S_{CD} + \Delta S_{DA} = 0,$$

as it should be.

## 2 Entropy change in the isobaric-isochoric-isothermic cycle of an ideal gas

Show that the entropy change in the cyclic process of an ideal gas that include an isobar, an isochor, and an isotherm is zero.

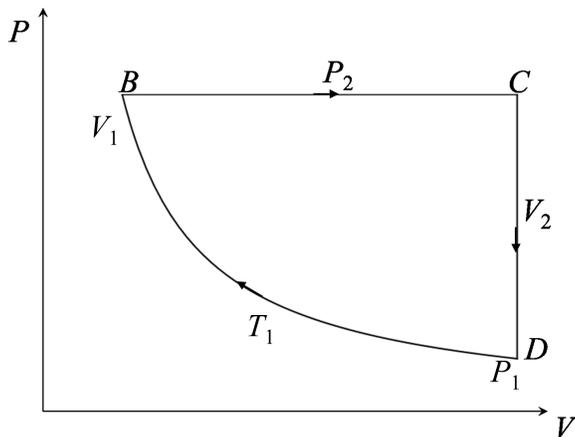


Figure 2: Isobar-isochor-isotherm cycle.

*Solution:* Using the results of the solution of the previous problem, one finds

$$\Delta S_{BC} = C_P \ln \frac{V_2}{V_1} > 0, \quad \Delta S_{CD} = C_V \ln \frac{P_1}{P_2} < 0.$$

In the isothermal process of an ideal gas  $dU = 0$  thus  $\delta Q = PdV$  and

$$dS = \frac{\delta Q}{T} = \frac{PdV}{T} = \nu R \frac{dV}{V}.$$

This yields

$$\Delta S_{DB} = \nu R \ln \frac{V_1}{V_2} < 0.$$

Using the equation of state of the ideal gas, on the ends of the isotherm one has

$$\frac{P_1}{P_2} = \frac{V_1}{V_2} \Rightarrow \Delta S_{CD} = C_V \ln \frac{V_1}{V_2}.$$

The total entropy change over the cycle is

$$\Delta S = \Delta S_{BC} + \Delta S_{CD} + \Delta S_{DB} = (C_P - C_V - \nu R) \ln \frac{V_2}{V_1} = 0,$$

as it should be.

## 3 Entropy of a perfect gas

Calculate the entropy of a perfect gas as a function of  $(V, T)$  by integration using  $S = \int \delta Q/T$ .

*Solution:* Define  $S(V_0, T_0) = S_0$  as a reference point and calculate the entropy  $S(V, T)$  via the integral of  $\delta Q/T$  over a path  $(V_0, T_0) \Rightarrow (V, T)$ , that is,

$$S(V, T) = S_0 + \int_{(V_0, T_0)}^{(V, T)} \frac{\delta Q}{T}.$$

As the the entropy is a state function, its value does not depend on the path. Thus one can choose the most convenient path, for instance,  $(V_0, T_0) \Rightarrow (V_0, T) \Rightarrow (V, T)$ . At the first stage only the temperature is changing while the work is zero, thus

$$\delta Q = dU = \left( \frac{\partial U}{\partial T} \right)_V dT = C_V dT.$$

Integration for the perfect gas ( $C_V = \text{const}$ ) proceeds as follows:

$$S(V_0, T) = S_0 + \int_{T_0}^T \frac{C_V dT}{T} = S_0 + C_V \ln \frac{T}{T_0}.$$

At the second stage  $T = \text{const}$ . As for the ideal gas  $U = U(T)$ , it does not change and  $\delta Q$  is only due to work,

$$\delta Q = PdV.$$

Using the equation of state of the ideal gas  $PV = \nu RT$  this can be rewritten as

$$\delta Q = \nu RT \frac{dV}{V}.$$

Now integration with  $T = \text{const}$  proceeds as follows:

$$S(V, T) = S(V_0, T) + \nu R \int_{V_0}^V \frac{dV}{V} = S_0 + C_V \ln \frac{T}{T_0} + \nu R \ln \frac{V}{V_0}.$$

Here the terms with  $T_0$  and  $V_0$  can be absorbed in the constant:

$$S(V, T) = C_V \ln T + \nu R \ln V + \text{const}.$$

Using  $C_P - C_V = \nu R$  (Meyer's relation) and  $\gamma = C_P/C_V$ , one can rewrite this formula as

$$S(V, T) = C_V (\ln T + (\gamma - 1) \ln V) + \text{const} = C_V \ln TV^{\gamma-1} + \text{const}.$$

The argument of the logarithm is constant in the adiabatic process,  $S = \text{const}$ , thus the result has an expected behavior and passes an error check.

## 4 Internal energy of a perfect gas in natural variables

Express the energy of a perfect gas in the natural variables,  $U = U(S, V)$ , and check relations

$$T = \left( \frac{\partial U}{\partial S} \right)_V, \quad -P = \left( \frac{\partial U}{\partial V} \right)_S, \quad \left( \frac{\partial T}{\partial V} \right)_S = - \left( \frac{\partial P}{\partial S} \right)_V.$$

*Solution:* In the  $V, T$  variables the energy of a perfect gas has the form

$$U = C_V T,$$

where a constant has been dropped for simplicity. The entropy of the perfect gas is given by

$$S = C_V \ln TV^{\gamma-1}, \tag{1}$$

where again a constant has been dropped. From here one can express  $T$  as a function of  $S$

$$T = \frac{1}{V^{\gamma-1}} \exp \left( \frac{S}{C_V} \right). \tag{2}$$

Thus the energy in its natural variables becomes

$$U(S, V) = \frac{C_V}{V^{\gamma-1}} \exp \left( \frac{S}{C_V} \right). \tag{3}$$

Note that  $U$  depends on the volume!

Now, using

$$dU = TdS - PdV$$

one can identify

$$T = \left( \frac{\partial U}{\partial S} \right)_V, \quad -P = \left( \frac{\partial U}{\partial V} \right)_S.$$

Let us check these relations. With the help of Eq. (2) one obtains.

$$\left( \frac{\partial U}{\partial S} \right)_V = \frac{1}{V^{\gamma-1}} \exp \left( \frac{S}{C_V} \right) = T,$$

as it should be. Further, using  $\gamma = C_P/C_V$  and  $C_P - C_V = \nu R$  one obtains

$$\left( \frac{\partial U}{\partial V} \right)_S = -\frac{(\gamma-1)C_V}{V^\gamma} \exp \left( \frac{S}{C_V} \right) = -\frac{\nu R}{V^\gamma} \exp \left( \frac{S}{C_V} \right).$$

Using Eq. (2)

$$\left(\frac{\partial U}{\partial V}\right)_S = -\frac{\nu RT}{V} = -\frac{PV}{V} = -P,$$

as it should be. Thus we have obtained

$$P = \frac{\nu R}{V^\gamma} \exp\left(\frac{S}{C_V}\right) \quad (4)$$

in the  $V, S$  variables. This formula also could be obtained from Eq. (1) and the equation of state, similarly to Eq. (2). Now, to check the Maxwell identity, Using Eq. (2) one calculates

$$\left(\frac{\partial T}{\partial V}\right)_S = -\frac{\nu R}{C_V V^\gamma} \exp\left(\frac{S}{C_V}\right).$$

On the other hand, from Eq. (4) one obtains

$$-\left(\frac{\partial P}{\partial S}\right)_V = -\frac{\nu R}{C_V V^\gamma} \exp\left(\frac{S}{C_V}\right) = \left(\frac{\partial T}{\partial V}\right)_S,$$

as expected.

## 5 Thermodynamic potentials $F$ and $G$ of the perfect gas

Express thermodynamic potentials  $F$  and  $G$  of the perfect gas in terms of their natural variables and check relations similar to those in the preceding problem.

*Solution:* Using the definition of  $F$  and the formulas for  $U$  and  $S$  of a perfect gas, one obtains

$$F = U - TS = C_V T - TC_V \ln TV^{\gamma-1} = -C_V T \ln(TV^{\gamma-1}/e). \quad (5)$$

Since

$$dF = -SdT - PdV,$$

one can identify

$$-S = \left(\frac{\partial F}{\partial T}\right)_V, \quad -P = \left(\frac{\partial F}{\partial V}\right)_T.$$

The entropy follows from Eq. (5) as

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = -C_V + C_V + C_V \ln TV^{\gamma-1} = C_V \ln TV^{\gamma-1}$$

that is a known result. The pressure is

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = \left(\frac{\partial (C_V T \ln V^{\gamma-1})}{\partial V}\right)_T = C_V T (\gamma-1) \left(\frac{\partial (\ln V)}{\partial V}\right)_T = \frac{C_V T (\gamma-1)}{V} = \frac{\nu RT}{V},$$

also a known result.

The Maxwell relation

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

is now checked as follows

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{\partial}{\partial V} C_V \ln TV^{\gamma-1} = C_V (\gamma-1) \frac{\partial \ln V}{\partial V} = \frac{\nu R}{V}.$$

On the other hand,

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\nu R}{V} = \left(\frac{\partial S}{\partial V}\right)_T,$$

as expected.

For the Gibbs thermodynamic potential  $G$  all calculations are parallel to those for  $F$ , only one has to express all the formulas via  $P$  instead of  $V$ , using the equation of state of the ideal gas.

## 6 Thermodynamics from $F$

The Helmholtz free energy of a certain gas has the form

$$F = -\frac{\nu^2 a}{V} - \nu RT \ln(V - \nu b) + J(T).$$

Find the equation of state of this gas, as well as its internal energy, entropy, heat capacities  $C_P$  and  $C_V$  and, in particular, their difference  $C_P - C_V$ .

*Solution:* To find the equation of state, one has to find  $P$  that will be a function of the native variables  $V, T$ :

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = -\frac{\nu^2 a}{V^2} + \frac{\nu RT}{V - \nu b}. \quad (6)$$

Rearranging this formula, one obtains

$$\left(P + \frac{\nu^2 a}{V^2}\right)(V - \nu b) = \nu RT, \quad (7)$$

the van der Waals equation of a non-ideal gas.

Next, the entropy is given by

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = \nu R \ln(V - \nu b) - J'(T).$$

Now the internal energy becomes

$$U = F + TS = -\frac{\nu^2 a}{V} + J(T) - TJ'(T).$$

The heat capacity  $C_V$  can be found as

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = -TJ''(T)$$

or as

$$C_V = T \left(\frac{\partial S}{\partial T}\right)_V = -TJ''(T).$$

Finding

$$C_P = T \left(\frac{\partial S}{\partial T}\right)_P$$

requires more work. An explicit way to do this is to express  $V$  in the form  $V = V(P, T)$  everywhere with the help of Eq. (7). However, this  $V$  is a solution of a cubic equation that is better to avoid. Also this method is inconvenient to study  $C_P - C_V$  because both heat capacities have to be functions of the same variables. Thus it is better to use the implicit method considering  $S = S(V, T)$  but with  $V = V(P, T)$ . Then one obtains

$$C_P = T \left(\frac{\partial S}{\partial T}\right)_V + T \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P = C_V + T \left(\frac{\partial S}{\partial V}\right)_T / \left(\frac{\partial T}{\partial V}\right)_P.$$

In this formula

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{\nu R}{V - \nu b},$$

whereas

$$\left(\frac{\partial T}{\partial V}\right)_P = \frac{1}{\nu R} \frac{\partial}{\partial V} \left(P + \frac{\nu^2 a}{V^2}\right)(V - \nu b) = \frac{1}{\nu R} \left[-\frac{2\nu^2 a}{V^3}(V - \nu b) + \left(P + \frac{\nu^2 a}{V^2}\right)\right].$$

Here one can eliminate  $P$  using Eq. (6) that yields

$$\left(\frac{\partial T}{\partial V}\right)_P = \frac{1}{\nu R} \left[-\frac{2\nu^2 a}{V^3}(V - \nu b) + \frac{\nu RT}{V - \nu b}\right].$$

Gathering the terms, one obtains

$$C_P - C_V = \frac{(\nu R)^2 T}{V - \nu b} / \left[-\frac{2\nu^2 a}{V^3}(V - \nu b) + \frac{\nu RT}{V - \nu b}\right],$$

further

$$C_P - C_V = \nu R \frac{\nu RT}{\nu RT - (2\nu^2 a/V^3)(V - \nu b)^2}$$

and, finally,

$$C_P - C_V = \frac{\nu R}{1 - \frac{2\nu^2 a(V - \nu b)^2}{\nu RT V^3}} > \nu R.$$

One can see that at high temperatures and large volumes the additional term in the denominator becomes small and the Meyer's relation for the ideal gas arises.