

Solutions to Problems in Recitation: 5

10/02/03

Problem 1

Consider an insulated and rigid chamber divided by one partition at the middle. One of the partitions is full with a gas. If the dividing wall suddenly breaks, please determine how the temperature of the system will change, as a function of properties such as specific heat, compressibilities, thermal conductivity, etc.

Solution 1

The total energy remains constant, since the system is thermally insulated and has rigid walls. Therefore, no heat and/or work can be transferred from the system to its surroundings, or vice-versa. Since the system is closed, there is also no change in the number of moles comprising the system. Based on this, we have that:

$$T_f - T_i = T(U, V_f, N) - T(U, V_i, N)$$

If the volume change is small,

$$dT = \left(\frac{\partial T}{\partial V} \right)_{U,N} dV$$

By using some of the mathematical rules for manipulating partial derivatives, we have:

$$dT = \frac{-\left(\frac{\partial U}{\partial V} \right)_{T,N} dV}{\left(\frac{\partial U}{\partial T} \right)_{V,N}} = -\frac{T \left(\frac{\partial S}{\partial V} \right)_{T,N} - P \left(\frac{\partial V}{\partial V} \right)_{T,N} dV}{T \left(\frac{\partial S}{\partial T} \right)_{V,N} - P \left(\frac{\partial V}{\partial T} \right)_{V,N}}$$

By using a Maxwell identity derived from the differential expression of the Helmholtz free energy ($\left(\frac{\partial S}{\partial V} \right)_{T,N} = \left(\frac{\partial P}{\partial T} \right)_{V,N}$), we modify the numerator of the previous expression. The denominator is simplified, since the p-v term gets cancelled by the 'constant volume condition':

$$dT = -\frac{T \left(\frac{\partial P}{\partial T} \right)_{V,N} - P \left(\frac{\partial V}{\partial V} \right)_{T,N} dV}{T \left(\frac{\partial S}{\partial T} \right)_{V,N}}$$

The first term of the numerator needs to be manipulated once again, in order to get more 'manageable' expressions:

$$dT = -\frac{-T \left(\frac{\partial V}{\partial P} \right)_{T,N} - P \left(\frac{\partial V}{\partial V} \right)_{T,N} dV}{T \left(\frac{\partial S}{\partial T} \right)_{V,N}}$$

Using the identities for α , κ_T and C_V , we have:

$$dT = -\frac{T \frac{\alpha \cdot V}{\kappa_T \cdot V} - P}{C_V} dV = \left(\frac{P}{C_V} - \frac{T\alpha}{C_V \kappa_T} \right) dV$$

For a *monoatomic* ideal gas we have:

$$\begin{aligned} PV &= NRT \\ C_V &= \frac{3}{2}NR \\ \alpha &= \frac{NR}{PV} \\ \kappa_T &= \frac{NR}{PV} \cdot \frac{T}{P} \end{aligned}$$

Substituting, and setting everything as a function of T , V , N and R , we thus have:

$$dT = \left(\frac{P}{C_V} - \frac{T\alpha}{C_V\kappa_T} \right) dV = \left(\frac{2}{3} \cdot \frac{T}{V} - \frac{2}{3} \cdot \frac{T}{V} \right) dV = 0$$

This would not hold for the case of real gases, for which the energy is not only a function of temperature, but also of the volume (for example, the *van der Waals* fluid.).

It is interesting to note that, *always* $C_V > 0$ and $\kappa_T > 0$ (necessary for the stability of a thermodynamic system). Usually, α is also positive (water is an exception, at $T \sim 0^\circ\text{C}$).

This means that a free expansion, for many kinds of materials, would generally lead to a decrease in the temperature of the system, provided the system is isolated from its surroundings (so it cannot exchange work, nor heat.).

Problem 2

In class we saw that, for an adiabatic pull, with force, F , the change in temperature under constant force is:

$$\left(\frac{\partial T}{\partial F} \right)_S = \frac{-L\alpha_L T}{C_F}$$

What is the relationship between C_F and C_P ?

Solution 2

Using the relationship

$$\left(\frac{\partial X}{\partial f} \right)_Z = \left(\frac{\partial X}{\partial f} \right)_Y + \left(\frac{\partial X}{\partial Y} \right)_f \cdot \left(\frac{\partial Y}{\partial f} \right)_Z$$

We find that

$$\frac{C_P - C_F}{T} = \left(\frac{\partial S}{\partial F} \right)_T \cdot \left(\frac{\partial F}{\partial T} \right)_P$$

From class, we also know that

$$\left(\frac{\partial S}{\partial F} \right)_T = \left(\frac{\partial L}{\partial T} \right)_F = L \cdot \alpha_L$$

$\left(\frac{\partial F}{\partial T} \right)_P$ can be manipulated using the chain rule:

$$\left(\frac{\partial F}{\partial T} \right)_P = \frac{\left(\frac{\partial F}{\partial L} \right)_P}{\left(\frac{\partial T}{\partial L} \right)_P} = \left(\frac{\partial F}{\partial L} \right)_P \cdot \left(\frac{\partial L}{\partial T} \right)_P$$

Since $K = \left(\frac{\partial F}{\partial L}\right)_P$ and $\left(\frac{\partial L}{\partial T}\right)_P = \left(\frac{\partial L}{\partial T}\right)_F = L \cdot \alpha_L$, we finally have:

$$\frac{C_P - C_F}{T} = L^2 \alpha_L^2 \cdot K$$

Thus, $C_P > C_F$. This means that the entropy of a system under isobaric condition is greater than when the system is subjected to tension along one direction.

Note that K is the Elastic Constant corresponding to the Hooke's Law. It can be easily related to the Young's Modulus: $K \sim E \cdot L$

Per mole, using

$$L_m \approx (V_m)^{1/3} \sim 1 \times 10^{-2} m/mol$$

And using $\alpha_L \sim 1 \times 10^{-6}$ and $K \sim 1 \times 10^9 \cdot L$
we have:

$$\frac{C_P - C_F}{T} \sim L_m^3 \cdot \alpha_L \cdot E \sim (1 \times 10^{-6}) \cdot (1 \times 10^{-6}) \cdot (1 \times 10^9) \sim 1 \times 10^{-3}$$