Problem set 4

Some slides

Problem 14

Helmholtz free energy for a monatomic ideal gas

$$F(T,V,N) = U - TS$$

$$U = \frac{3}{2} NRT$$

$$\frac{U}{U_0} = \frac{NT}{N_0 T_0}$$

$$S = \frac{N}{N_0} S_0 + NR \ln \left[\left(\frac{U}{U_0}\right)^{3/2} \frac{V}{V_0} \left(\frac{N}{N_0}\right)^{-5/2}\right]$$

$$S = \frac{N}{N_0} S_0 + NR \ln \left(\left(\frac{T}{T_0}\right)^{3/2} \frac{V}{V_0} \left(\frac{N}{N_0}\right)^{-1}\right)$$

$$\boxed{F(T,V,N) = \frac{3}{2} NRT - \frac{N}{N_0} S_0 T - NRT \ln \left(\left(\frac{T}{T_0}\right)^{3/2} \frac{V}{V_0} \left(\frac{N}{N_0}\right)^{-1}\right)}$$

Supporting notes

Two ways to write the Ideal Gas equation of state $U = U(T, V, N)$

$$U = \frac{3}{2}NRT \qquad\qquad U = \frac{N}{N_0}U_0 + \frac{3}{2}NR(T - T_0)$$

$$\Downarrow \qquad\qquad\qquad \Downarrow$$

where $U(T_0, N_0) = \frac{3}{2}N_0RT_0$ $\qquad U(T_0, N_0) = U_0$

Ergo, the two agree if we define that: $U_0 \equiv \frac{3}{2}N_0RT_0$

Supporting notes

Two ways to write the Ideal Gas equation of state $U = U(T, V, N)$

$$\boxed{U = \frac{3}{2} NRT}$$

$$\boxed{U = \frac{N}{N_0} U_0 + \frac{3}{2} NR(T - T_0)}$$

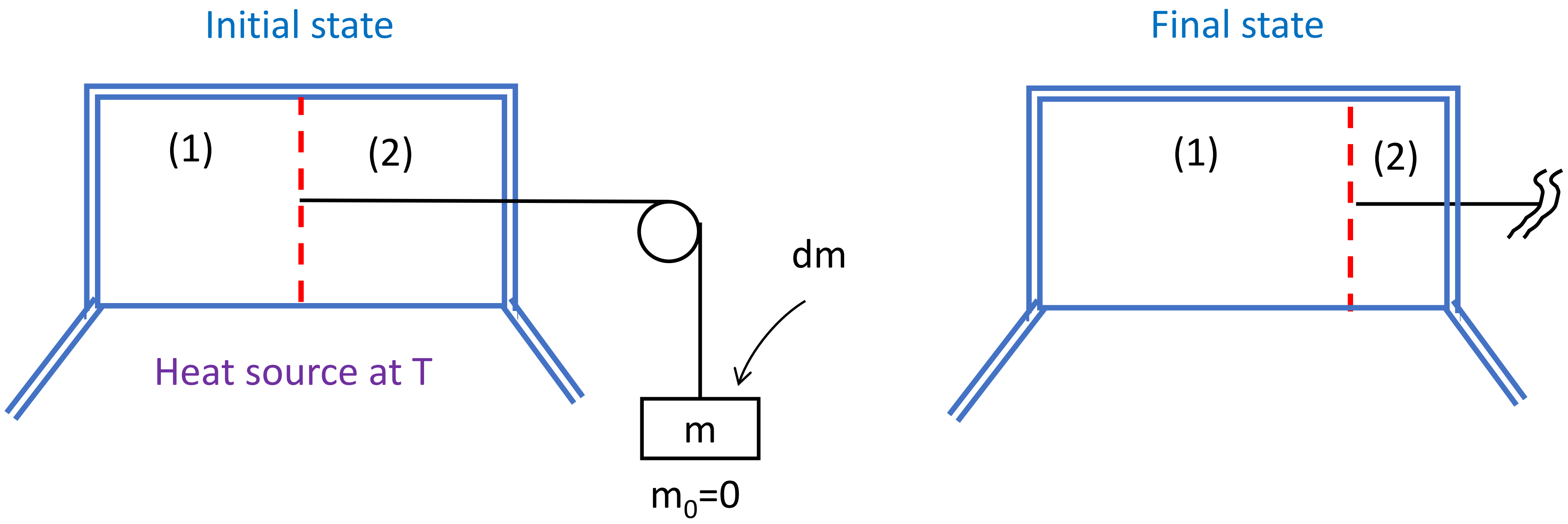
$$U_0 = U(T_0, N_0) = \frac{3}{2} N_0 R T_0$$

identical

$$\boxed{F(T, V, N) = \frac{3}{2} NRT - \frac{N}{N_0} S_0 T - NRT \ln\left(\left(\frac{T}{T_0}\right)^{3/2} \frac{V}{V_0} \left(\frac{N}{N_0}\right)^{-1}\right)}$$

$$\boxed{F(T, V, N) = \frac{N}{N_0} U_0 + \frac{3}{2} NR(T - T_0) - \frac{N}{N_0} S_0 T - NRT \ln\left[\left(\frac{T}{T_0}\right)^{3/2} \frac{V}{V_0} \left(\frac{N}{N_0}\right)^{-1}\right]}$$

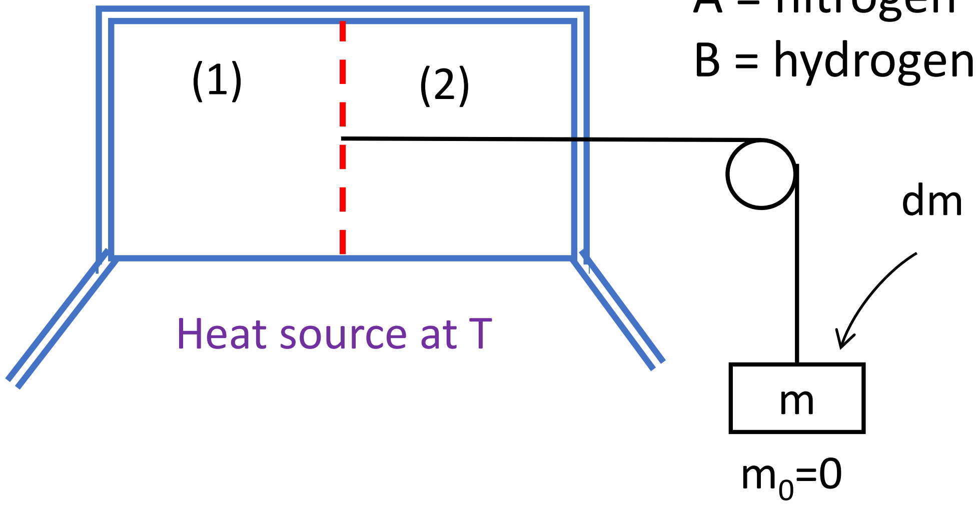
Problem 15



Variable	Symbol	Initial value	Final value
Volume of subsystem 1	$V^{(1)}$	10 L	15 L
Volume of subsystem 2	$V^{(2)}$	10 L	5 L
Moles of nitrogen in sys.1	$N_A^{(1)}$	1/2 mol	1/2 mol
Moles of nitrogen in sys.2	$N_A^{(2)}$	1/2 mol	1/2 mol
Moles hydrogen in sys.1	$N_B^{(1)}$	1/2 mol	3/4 mol
Moles hydrogen in sys.2	$N_B^{(2)}$	1/2 mol	1/4 mol

A = nitrogen
B = hydrogen

Problem 15 **Method 2** $W = -\Delta F$ $F = F^{(1)} + F^{(2)}$



A = nitrogen
B = hydrogen

$$F = F^{(1)}(T, V^{(1)}, N_A^{(1)}, N_B^{(1)}) + F^{(2)}\left(T, V^{(2)}, N_A^{(2)}, N_B^{(2)}\right)$$

Therefore, $F = F\left(T, V^{(1)}, V^{(2)}, N_A^{(1)}, N_A^{(2)}, N_B^{(1)}, N_B^{(2)}\right)$
...although not all these variables are independent in this particular problem (closure relations).

F of a binary mixture of diatomic ideal gases: FIRST FOR A MONOCOMPONENT DIATOMIC GAS

See problem 14

$$F(T, V, N) = \frac{5}{2} NRT - \frac{N}{N_0} S_0 T - NRT \ln\left(\left(\frac{T}{T_0}\right)^{5/2} \frac{V}{V_0} \left(\frac{N}{N_0}\right)^{-1}\right)$$

We define: For one component ($j = A, B$)

$$F_j(T, V, N_j) \equiv \frac{5}{2} N_j RT - \frac{N_j}{N_0} S_{0j} T - N_j RT \ln\left(\left(\frac{T}{T_0}\right)^{5/2}\right) - N_j RT \ln\left(\frac{V}{V_0}\left(\frac{N_j}{N_0}\right)^{-1}\right)$$

We claim that for an IDEAL GAS MIXTURE (no interactions):

$$\boxed{F^{(\mathrm{i})}\left(T, V^{(\mathrm{i})}, N_A^{(\mathrm{i})}, N_B^{(\mathrm{i})}\right) = F_A^{(\mathrm{i})} + F_B^{(\mathrm{i})}}$$

Problem 15

Method 2

$$W = -\Delta F \qquad F = F^{(1)} + F^{(2)}$$

$$\Delta F = \Delta\left(F^{(1)} + F^{(2)}\right) = \Delta\left(F_A^{(1)} + F_B^{(1)} + F_A^{(2)} + F_B^{(2)}\right)$$

A = nitrogen
B = hydrogen

However, for the hydrogen: $\Delta\left(F_B^{(1)} + F_B^{(2)}\right) = 0$

Therefore, only nitrogen contributes:

$$\Delta F = \Delta\left(F^{(1)} + F^{(2)}\right) = \Delta\left(F_A^{(1)} + F_A^{(2)}\right)$$

$$F_A(T, V, N_A) \equiv \underbrace{\frac{5}{2} N_A R T - \frac{N_A}{N_0} S_{0j} T - N_A R T \ln\left(\left(\frac{T}{T_0}\right)^{5/2}\right)}_{N_A \text{ and } T \text{ are constant; ergo, these contribute zero to } \Delta F.} - N_A R T \ln\left(\frac{V}{V_0}\left(\frac{N_A}{N_0}\right)^{-1}\right)$$

In each subsystem

Problem 15

$$\Delta F = \Delta\left(F_A^{(1)} + F_A^{(2)}\right)$$

$$= -N_A^{(1)} RT\left(\ln\left(\frac{N_0}{V_0 N_A^{(1)}} V_f^{(1)}\right) - \ln\left(\frac{N_0}{V_0 N_A^{(1)}} V_i^{(1)}\right)\right)$$

$$- N_A^{(2)} RT\left(\ln\left(\frac{N_0}{V_0 N_A^{(2)}} V_f^{(2)}\right) - \ln\left(\frac{N_0}{V_0 N_A^{(2)}} V_i^{(2)}\right)\right)$$

$$= \frac{N_A}{2} RT \ln\left(\frac{V_i^{(1)}}{V_f^{(1)}} \frac{V_i^{(2)}}{V_f^{(2)}}\right)$$