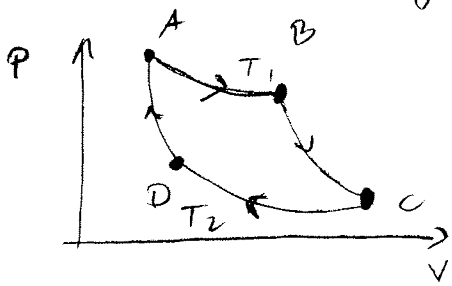
HW #1 Solutions

(1) Explicitly calculate the efficiency of the Carnot-cycle for the ideal gas.




$A \to B$ isothermal, $T_{high}$

$B \to C$ adiabatic

$C \to D$ isothermal, $T_{low}$

$D \to A$ adiabatic

$$\eta = 1 - \frac{Q_{high}}{Q_{low}}$$

since ideal gas $dE = 0 = \delta Q + \delta W$ along an isotherm

$$Q_{high} = NkT_{high} \ln \frac{V_B}{V_A}$$ (from class)

$$Q_{low} = NkT_{low} \ln \frac{V_C}{V_D}$$

$B \to C$ adiabatic process $T_{high} V_B^{\gamma-1} = T_{low} V_C^{\gamma-1}$

$D \to A$ adiabatic process $T_{low} V_D^{\gamma-1} = T_{high} V_A^{\gamma-1}$

$\Rightarrow \left(\frac{V_C}{V_D}\right)^{\gamma-1} = \left(\frac{V_B}{V_A}\right)^{\gamma-1}$

i.e., $\boxed{\frac{V_C}{V_D} = \frac{V_B}{V_A}}$

$$\eta = 1 - \frac{Q_{low}}{Q_{high}} = 1 - \frac{NkT_{low} \ln \frac{V_C}{V_D}}{NkT_{high} \ln \frac{V_B}{V_A}} = 1 - \frac{T_{low}}{T_{high}}$$

② <u>Entropy for V.d.W. gas</u> (for fixed N)

(∗) $E = \frac{3}{2} NkT - N\frac{N}{V} a$ energy

(∗∗) $\left(P + a\frac{N^2}{V^2}\right)(V - bN) = NkT$ equation of state

$S = S(E, V, N)$ $dS = \frac{1}{T} dE + \frac{P}{T} dV$

from (∗): $dE = \frac{3}{2} Nk\, dT + \frac{N^2}{V^2} a\, dV$

from (∗∗): $P = \frac{NkT}{V-bN} - a\frac{N^2}{V^2}$

$$dS = \frac{3}{2} Nk \frac{dT}{T} + \cancel{\frac{N^2}{V^2} a \frac{dV}{T}} + \frac{Nk}{V-bN} dV - \cancel{\frac{N^2}{V^2}\frac{a}{T} dV} =$$

$$= \frac{3}{2} Nk \frac{dT}{T} + Nk \frac{dV}{V-bN}$$

$$S(T,V) = \frac{3}{2} Nk \ln T + Nk \ln(V - bN) + S_0$$

(we cannot say more about $S_0$ at this point, but we can uniquely express the total change in $S$ as a func. of $T, V$:

$$\Delta S = S(T_2, V_2) - S(T_1, V_1) = \frac{3}{2} Nk \ln T_2/T_1 + Nk \ln \frac{V_2 - bN}{V_1 - bN}$$

or as a function of $E, V$:

$$\Delta S = S(E_2, V_2) - S(E_1, V_1) = \frac{3}{2} Nk \ln \frac{\left(E_2 + N\frac{N}{V_2}a\right)}{\left(E_1 + N\frac{N}{V_1}a\right)} + Nk \ln \frac{V_2 - bN}{V_1 - bN}$$

note that $C_V = \left(\frac{\partial E}{\partial T}\right)_V = \frac{3}{2} Nk$ for the V.d.W gas as well

so we can write:

$$\Delta S = C_V \ln\left(\frac{E_2 + \frac{N^2 a}{V_2}}{E_1 + \frac{N^2 a}{V_1}}\right) + Nk \ln\left(\frac{V_2 - bN}{V_1 - bN}\right)$$

③ Determine the T–V and P–V eq. for quasistatic adiabatic process for V.d.W gas.

$$dE = \delta Q + \delta W$$

$$dE + p\,dV = 0$$

$$0 = C_V\,dT + \cancel{\frac{N^2}{V^2}a\,dV} + \frac{NkT}{V-bN}\,dV - \cancel{a\frac{N^2}{V^2}\,dV}$$

$$C_V\frac{dT}{T} + Nk\frac{dV}{V-bN} = 0$$

$$\ln\left(T^{C_V}\cdot(V-bN)^{Nk}\right) = \text{const}$$

$$T\,(V-bN)^{Nk/C_V} = \text{const}$$

or using the equation of state: $\left(P + a\frac{N^2}{V^2}\right)(V-bN) = NkT$

$$\Rightarrow \left(P + a\frac{N^2}{V^2}\right)(V-bN)^{\frac{Nk}{C_V}+1} = \text{const.}$$

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$$dE = T\,dS - p\,dV$$

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

we need to find $\left(\frac{\partial S}{\partial V}\right)_T$. Use Helmholtz Free energy:

$$dF = -S\,dT - p\,dV \qquad F(T,V)$$

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

$$\frac{\partial^2 F}{\partial V\partial T} = -\left(\frac{\partial S}{\partial V}\right)_T \qquad \frac{\partial^2 F}{\partial T\partial V} = -\left(\frac{\partial P}{\partial T}\right)_V$$

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

Thus,

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

i.e. internal energy and equation of state are not independent

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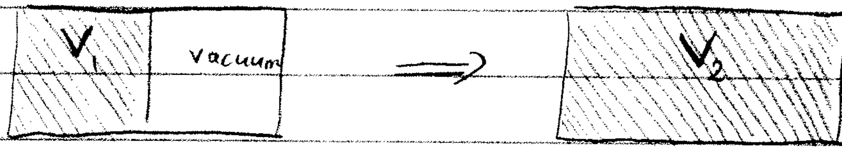
## The Joule (of free expansion) process




$V_1 < V_2$

- thermally isolated : $\delta Q = 0$
- since expanding into vacuum, no work done : $\delta W = 0$

I law: $dE = \delta Q + \delta W = 0$ , i.e., the total energy must be constant during this process

$$dE = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV \qquad dE = 0 \quad (E = \text{const.})$$

$$\Rightarrow \quad \left(\frac{\partial T}{\partial V}\right)_E = -\frac{\left(\frac{\partial E}{\partial V}\right)_T}{\left(\frac{\partial E}{\partial T}\right)_V}$$

by definition: $\left(\frac{\partial E}{\partial T}\right)_V = C_V$

from problem (2): $\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$

$$\left(\frac{\partial T}{\partial V}\right)_E = -\frac{T\left(\frac{\partial P}{\partial T}\right)_V - P}{C_V}$$

Thus, at constant $E$:
(if $C_V$ has no $T$-dependence)

$$\boxed{\Delta T = T_2 - T_1 = -\int_{V_1}^{V_2} \frac{T\left(\frac{\partial P}{\partial T}\right)_V - P}{C_V}\, dV}$$

⑥ cont'd

a) for the ideal gas:

$$PV = NkT \qquad P = \frac{Nk}{V}T$$

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

$$\Rightarrow \quad T\left(\frac{\partial P}{\partial T}\right)_V - P = T\frac{Nk}{V} - P \equiv \emptyset$$

thus, $\Delta T = 0$

b) v.d.W gas:

$$\left(P + \frac{N^2}{V^2}a\right)\left(V - Nb\right) = NkT \qquad E = \frac{3}{2}NkT - N\left(\frac{N}{V}\right)a$$

$$\Downarrow$$

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = \frac{3}{2}Nk$$

$$P = \frac{NkT}{V-Nb} - a\frac{N^2}{V^2}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{Nk}{V-Nb} \quad \Rightarrow \quad T\left(\frac{\partial P}{\partial T}\right)_V = \frac{NkT}{V-Nb}$$

$$T\left(\frac{\partial P}{\partial T}\right)_V - P = a\frac{N^2}{V^2}$$

$$\Delta T = -\int_{V_1}^{V_2} \frac{a\frac{N^2}{V^2}}{C_V}\,dV = -\frac{aN^2}{\frac{3}{2}Nk}\int_{V_1}^{V_2}\frac{dV}{V^2} \Rightarrow$$

$$= \frac{2}{3}\frac{aN}{k}\left.\frac{1}{V}\right|_{V_1}^{V_2} = \frac{2}{3}\frac{aN}{k}\underbrace{\left(\frac{1}{V_2} - \frac{1}{V_1}\right)}_{<0} < 0$$

Thus $\Delta T < 0$, the free expansion for the v.d.W gas results in cooling.