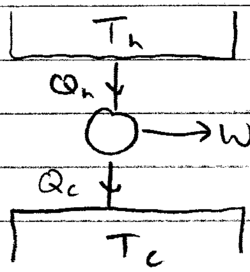
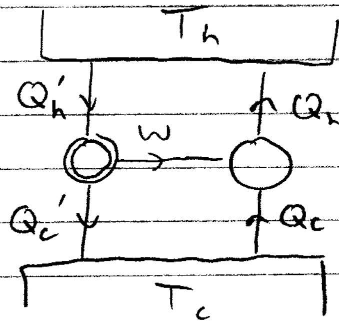
1. A Carnot engine is a <u>reversible</u> process that does work W while extracting heat Q_h from a reservoir at temp T_h, and emitting heat Q_c into a reservoir at temp T_c.



<u>Efficiency</u> $\eta \equiv \frac{W}{Q_h}$

Suppose another engine were more efficient. Then it could perform work W with heat input $\underline{Q_h' < Q_h}$

Use the output of the new engine to drive the input of a Carnot engine operating in reverse:

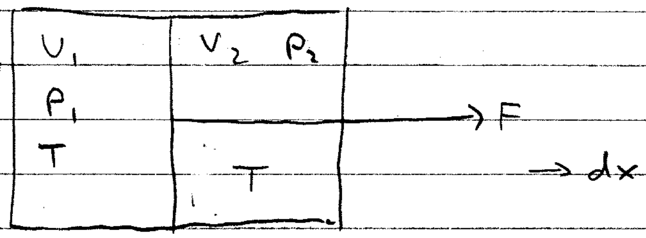


Since $Q_h > Q_h'$, net effect is to transfer heat $\Delta Q = Q_h - Q_h'$ from T_c to T_h.

However, the second law says that heat only flows spontaneously from higher to lower T.

Therefore, the supposed engine violates the second law.

2.



Say area of piston is A

Pull string by dx, do work $dW = F\,dx$

Need $F = A(P_2 - P_1)$ to balance forces

So $$W = \int F\,dx$$

$$= \int (P_2 - P_1)\, A\,dx$$

Use $A\,dx = dV_1 = -dV_2$

$$W = -\int P_2\,dV_2 - \int P_1\,dV_1 \quad \text{as expected}$$

For isothermal process, $P = \dfrac{NkT}{V}$

$$W = -kT\left\{ N_2 \int_{V_{2i}}^{V_{2f}} \frac{1}{V}\,dV + N_1 \int_{V_{1i}}^{V_{1f}} \frac{1}{V}\,dV \right\}$$

where initial volumes are V_{1i}, V_{2i}

final volumes V_{1f}, V_{2f}

$$\boxed{W = -kT\left\{ N_2 \ln \frac{V_{2f}}{V_{2i}} + N_1 \ln \frac{V_{1f}}{V_{1i}} \right\}}$$

Helmholtz free energy $A = E - TS$

For ideal gas, $S = f(T) + N k_B \ln V$

Since $T = \text{const}$, $\Delta A = -T\Delta S = -NkT\left[\ln V_f - \ln V_i\right]$

So $\Delta A = \Delta A_1 + \Delta A_2 = -kT\left[N_1 \ln \frac{V_{1f}}{V_{1i}} + N_2 \ln \frac{V_{2f}}{V_{2i}}\right]$

$= W$

as claimed.

3. a) $G = \sum_i G_i$

$$= \mu^o_{AB} N_{AB} + kT N_{AB} \ln X_{AB}$$

$$+ \mu^o_{CD} N_{CD} + kT N_{CD} \ln X_{CD}$$

$$+ \mu^o_{AC} N_{AC} + kT N_{AC} \ln X_{AC}$$

$$+ \mu^o_{BD} N_{BD} + kT N_{BD} \ln X_{BD}$$

Express N's in terms of ξ:

Know that $N_{AB} + N_{AC} = N$, since N atoms of species A

So $\xi = \frac{N_{AC}}{N} \Rightarrow \boxed{N_{AC} = \xi N}$

Also clear that $N_{BD} = N_{AC}$, since both molecules formed together

So $\boxed{N_{BD} = \xi N}$

Then $\boxed{N_{AB} = N - N_{AC} = (1-\xi) N}$

and $\boxed{N_{CD} = N_{AB} = (1-\xi) N}$

So

$$G = N \Big\{ \mu^o_{AB} (1+\xi) + \mu^o_{CD} (1-\xi) + \mu^o_{AC} \xi + \mu^o_{BD} \xi$$

$$+ kT \left[(1-\xi) \ln X_{AB} + (1-\xi) \ln X_{CD} + \xi \ln X_{AC} + \xi \ln X_{BD} \right] \Big\}$$

Note that total pressure P and temperature T are constant, so μ_i°'s are constant.

However, due to internal energies, know

$$\mu^\circ_{AB} + \mu^\circ_{CD} = \mu^\circ_{AC} + \mu^\circ_{BD} - \varepsilon$$

Also have $x_i = \dfrac{N_i}{N_{AB}+N_{AC}+N_{BD}+N_{CD}} = \dfrac{N_i}{2N}$

So $x_{AB} = x_{CD} = \frac{1}{2}(1-\xi)$

$x_{AC} = x_{BD} = \frac{1}{2}\xi$

So

$$G = N\Big\{\mu^\circ_{AB} + \mu^\circ_{CD} + \xi(\mu^\circ_{AC} + \mu^\circ_{BD} - \mu^\circ_{AB} - \mu^\circ_{CD})$$
$$+ kT\Big[2(1-\xi)\ln\tfrac{1}{2}(1-\xi)$$
$$+ 2\xi\ln\tfrac{1}{2}\xi\Big]\Big\}$$

$$\boxed{\begin{aligned} G = N\Big\{&\mu^\circ_{AB} + \mu^\circ_{CD} + \varepsilon\xi \\ &2kT\Big[\ln\tfrac{1}{2} + (1-\xi)\ln(1-\xi) \\ &+ \xi\ln\xi\Big]\Big\}\end{aligned}}$$

b) Set $\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = 0$

$$\varepsilon + 2kT\left[-\ln(1-\xi) - 1 + \ln \xi + 1\right] = 0$$

$$\varepsilon + 2kT \ln \frac{\xi}{1-\xi} = 0$$

$$\ln \frac{\xi}{1-\xi} = -\frac{\varepsilon}{2kT}$$

$$\frac{\xi}{1-\xi} = e^{-z} \qquad z = \frac{\varepsilon}{2kT}$$

$$\xi = e^{-z}(1-\xi)$$

$$\xi(1+e^{-z}) = e^{-z}$$

$$\xi = \frac{e^{-z}}{1-e^{-z}}$$

$$\boxed{\xi = \frac{1}{e^{\varepsilon/2kT} - 1}}$$

4. a) $\left(P + \frac{a}{v^2}\right)(v - b) = kT$ $\qquad v = \frac{V}{N}$

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

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

$$= \left(\frac{\partial}{\partial T}\left(\frac{\partial E}{\partial V}\right)_T\right)_V \qquad \text{(all at fixed } N\text{)}$$

But $\left(\frac{\partial E}{\partial V}\right)_T$ is related to pressure

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

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

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

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

Have
$$P = \frac{kT}{v-b} - \frac{a}{v^2}$$

$$T\left(\frac{\partial P}{\partial T}\right)_V = \frac{kT}{v-b}$$

So $\left(\frac{\partial E}{\partial V}\right)_T = \frac{kT}{v-b} - \left[\frac{kT}{v-b} - \frac{a}{v^2}\right] = +\frac{a}{v^2}$

and thus $\left(\frac{\partial}{\partial T}\left(\frac{\partial E}{\partial V}\right)_T\right)_V = 0$

$$\Rightarrow \boxed{\left(\frac{\partial C_V}{\partial V}\right)_T = 0} \quad ✓$$

b) See that C_V is independent of V

But in large V limit, interactions are negligible and any gas looks ideal

Heat capacity of a monatomic ideal gas

$$C_V^{(ideal)} = \frac{3}{2} N k_B$$

So, conclude that $\boxed{C_V = \frac{3}{2} N k_B}$

c) Have $dE = \left(\frac{\partial E}{\partial T}\right)_{V,N} dT + \left(\frac{\partial E}{\partial V}\right)_{T,N} dV + \left(\frac{\partial E}{\partial N}\right)_{T,V} dN$

we know $\left(\frac{\partial E}{\partial T}\right)_{V,N} = \frac{3}{2} N k_B$

and we got $\left(\frac{\partial E}{\partial V}\right)_{T,N} = \frac{aN^2}{V^2}$ in (a)

What about $\left(\frac{\partial E}{\partial N}\right)_{V,T}$?

Say $\left(\frac{\partial E}{\partial N}\right)_{V,T} = K(T,V,N)$

Then $\frac{\partial K}{\partial V} = \frac{\partial}{\partial N}\left(\frac{aN^2}{V^2}\right) = \frac{2Na}{V^2}$

and therefore $K = -\frac{2Na}{V} + f(N,T)$

But as $V \to \infty$, know that $K \to \frac{3}{2} k_B T$, like ideal gas

So, $K = -\frac{2Na}{V} + \frac{3}{2} k_B T$

So,
$$dE = \frac{3}{2} N k_B \, dT + \frac{aN^2}{V^2} \, dV + \left(\frac{3}{2} k_B T - \frac{2Na}{V} \right) dN$$

and get
$$\boxed{E = \frac{3}{2} N k_B T - \frac{aN^2}{V} + \text{const}}$$

(Note however, I had sign of a term wrong in problem statement!)