

1. Consider the Carnot-cycle for the *ideal gas*. Show explicitly, that

$$\frac{Q_{low}}{Q_{high}} = \frac{T_{low}}{T_{high}},$$

i.e., the efficiency of this engine, using ideal gas as the working substance, is $\eta = 1 - \frac{T_{low}}{T_{high}}$. (This, of course, just provides an example for Carnot's principle, that is, all reversible engines operating between the same pair of temperatures have the above optimal efficiency.)

Hint: based on the equation of state, the expression for the internal energy, and the definition of work, find explicitly the heat transferred during the isothermal segments of the cycle, Q_{high} and Q_{low} .

Ideal gas : $PV = NkT$

Internal energy $E = \frac{3}{2}NkT \rightarrow V_1 = \frac{NkT}{P}$

Work $= Q_{1 \rightarrow 2} = NkT \ln\left(\frac{V_1}{V_2}\right)$

Isothermal high

$$Q_h = NkT_h \ln\left(\frac{V_1}{V_2}\right) \quad Q = 0 \text{ for}$$

Isothermal low

$$Q_L = NkT_L \ln\left(\frac{V_3}{V_4}\right) \quad \begin{matrix} \text{adiabatic parts} \\ (\text{compression/expansion}) \end{matrix}$$

Adiabatic Expansion

$$W_{\text{expansion}} = -W_{\text{compression}}$$

$$\Delta_e E = W_e = \int_{T_h}^{T_L} \frac{3}{2} Nk dT$$

$$\therefore W_e + W_c = 0$$

Compression

$$W_{\text{net}} = W_e + W_c - Q_h - Q_L$$

$$\Delta_c E = W_c = \int_{T_h}^{T_L} \frac{3}{2} Nk dT$$

$$W_{\text{net}} = -Q_h - Q_L$$

1st Law :

$$W = Q - \Delta E_{\text{int}}$$

$$W = (Q_h - Q_L)$$

$$W_{\text{net}} = W_h + W_L$$

\nearrow

\nwarrow agrees

$$\eta = \frac{W_{out}}{Q_{in}} \rightarrow \frac{Q_h - Q_c}{Q_h} \quad \frac{Q_2}{Q_h} = \frac{Nk T_2 \ln(\frac{V_3}{V_4})}{Nk T_h \ln(\frac{V_1}{V_2})}$$

$$\Leftrightarrow 1 - \frac{Q_c}{Q_h} = \eta \quad \Leftrightarrow \frac{T_2}{T_h} \frac{\ln \frac{V_3}{V_4}}{\ln \frac{V_1}{V_2}}$$

adiabatic process:

$$\delta Q = 0$$

$$\eta = 1 - \frac{T_2}{T_h} \frac{\ln \frac{V_3}{V_4}}{\ln \frac{V_1}{V_L}}$$

$$dE = C_v dT$$

$$C_v dT = -P dV$$

$$C_v \frac{dT}{T} = -\frac{Nk dr}{V}$$

$$\frac{dT}{T} = -\left(\frac{C_p - 1}{C_v}\right) \frac{dV}{V}$$

$$\ln(T) + \ln(V^{r-1}) = \text{const}$$

$$T \cdot V^{r-1} = \text{const}$$

$$P = \frac{NkT}{V}$$

expansion

compression

$$\frac{T_h V_1^{r-1}}{T_L V_2^{r-1}} = \frac{T_C V_3^{r-1}}{T_C V_4^{r-1}}$$

$$\frac{V_1}{V_L} = \frac{V_3}{V_4}$$

* Subbing into η

$$T_h V_1^{r-1} = T_C V_3^{r-1} \quad (\text{expansion})$$

$$1 - \frac{Q_c}{Q_h} = 1 - \frac{T_C}{T_h} \frac{\ln \left(\frac{V_3}{V_4} \right)}{\ln \left(\frac{V_1}{V_L} \right)}$$

$$T_C V_4^{r-1} = T_h V_2^{r-1} \quad (\text{compression})$$

$$\Leftrightarrow T_h V_2^{r-1} = T_C V_4^{r-1}$$

$$1 - \frac{Q_c}{Q_h} = 1 - \frac{T_C}{T_h}$$

$$\frac{Q_c}{Q_n} = \frac{T_c}{T_h}$$

2. Using the equation of state and the expression for the internal energy, find the entropy of the van der Waals gas, $S(E, V)$ (the number of particles N is fixed). (Hint: you may first try to obtain $S(T, V)$ and then using again the expression for the internal energy for the v.d.W. gas, obtain $S(E, V)$.

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

Deriving $S(T, P)$

$$dS = \frac{1}{T} dE + \frac{P}{T} dV - \frac{\mu}{T} dN$$

$$PV + \frac{\alpha N^2}{V} - PNb + \frac{\alpha b N^3}{V^2} = NkT$$

$$P(V - Nb) = NkT + \frac{\alpha N^2}{V} + \frac{\alpha b N^3}{V^2}$$

$$P = \frac{NkT}{V-nb} + \frac{\alpha n^2}{V^2}$$

$$dS = \frac{1}{T} dE + \left(\frac{NkT}{V-nb} + \frac{\alpha n^2}{V^2} \right) \frac{1}{T} dV$$

$$dS = \frac{1}{T} \left(\frac{3}{2} NkT + N\left(\frac{N}{V}\right)a \right) + \left(\frac{NkT}{V-nb} + \frac{\alpha n^2}{V^2} \right) \frac{1}{T} dV$$

$$dS = \frac{1}{T} \frac{3}{2} N k dT - \left[\frac{N}{T} \left(\frac{\alpha N}{V} \right) \right] dV + \left(\frac{Nk}{V-Nb} + \frac{\alpha N^2}{TV^2} \right) dV$$

$$\int dS = \int \frac{1}{T} \frac{3}{2} N k dT - \int \frac{N}{T} \left(\frac{\alpha N}{V} \right) dV + \frac{Nk}{V-Nb} + \frac{\alpha N^2}{TV^2} dV$$

$$S(T, V) = \frac{3}{2} N k \ln(T) - \frac{\alpha N^2}{T} \ln(V) + N k \ln(V-Nb) - \frac{\alpha N^2}{TV}$$

$$\langle E \rangle = \frac{3}{2} N k \ln(T) - \frac{\alpha N^2}{T} \left(\ln(V) + N k \ln(V-Nb) - \frac{1}{V} \right)$$

finding $S(E, V)$

$$E = \frac{3}{2} N k T - N \left(\frac{N}{V} \right) \alpha$$

$$\left(E + \frac{N^2 \alpha}{V} \right) \frac{2}{3 N k} = T$$

$$S(E, V) = \frac{3}{2} N k \ln \left(E + \frac{N^2 \alpha}{V} \right) - \alpha N^2 \frac{3 N k}{2} \left(\frac{1}{E} + \frac{V}{N^2 \alpha} \right) \left(\ln(V) + N k \ln(V-Nb) - \frac{1}{V} \right)$$

$$S(E, V) = \frac{3}{2} N k \ln \left(E + \frac{N^2 \alpha}{V} \right) - \left(\frac{3 \alpha N^3 k}{2 E} + \frac{3 N k V}{2} \right) \left(\ln(V) + N k \ln(V-Nb) - \frac{1}{V} \right)$$

3. Determine the relationship between T and V for the (quasistatic) **adiabatic** process for the v.d.W. gas. Then obtain the relationship between P and V . Sketch $P(V)$ for the above process and also sketch $P(V)$ for the isothermal process of the v.d.W. gas (on the same graph), starting at the same temperature and volume. Compare them and discuss your findings.

$$\delta E = \cancel{\delta W + \delta Q} \quad (\text{adiabat})$$

$$\delta W = -P \delta V$$

$$\delta E = -P \delta V \rightarrow 0 = \delta E + P \delta V$$

$$\left(P + \frac{\alpha N^2}{V^2}\right)(V - Nb) = NkT \quad \text{and} \quad E = \frac{3}{2}NkT - N\left(\frac{N}{V}\right)\alpha$$

$$C_V = \frac{3}{2}Nk$$

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

$$P = \frac{NkT}{V-nb} + \frac{\alpha n^2}{V^2}$$

$$\delta E = \frac{3}{2}Nk\delta T + \alpha N^2 \ln|V| \delta V = P \delta V = \left[\frac{NkT}{V-nb} + \frac{\alpha n^2}{V^2} \right] \delta V$$

$$0 = C_V \delta T + \frac{NkT}{V-nb} \delta V$$

$$P = T \frac{Nk}{V-nb} + \frac{\alpha n^2}{V^2}$$

$$0 = \frac{C_V}{T} \delta T + Nk \frac{1}{V-nb} \delta V$$

$$T = P \frac{V-nb}{Nk} - \frac{\alpha n^2}{V^2}$$

$$\phi = \ln|T|^{\frac{C_V}{T}} + \ln|V - Nb|^{Nk}$$

$$C = T (V - Nb)^{NkC_V}$$

$$C = \left(P \left(\frac{V-nb}{Nk} \right) - \frac{an^2}{V^2} \right) (V-Nb)^{NkC_V}$$



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* As volume increases, pressure falls faster in the adiabatic case

4. Prove the following important and general thermodynamic relationship:

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

Note that this relationship is *independent* of the specific substance. It explicitly shows that the equation of state $P(T, V)$ and the internal energy $E(T, V)$ are not independent of each other.

Hint: start with the First Law, $dE = TdS - PdV$, then use the appropriate Maxwell relationship to obtain the desired result.

$$dE = TdS - PdV \quad \text{at } 1st \text{ law}$$

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

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

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

5. The Joule process (or free expansion). Consider a gas, which expands into a vacuum from V_1 to V_2 while the system is thermally isolated.

(a) Show that the temperature change during this process is given by

$$\Delta T = T_2 - T_1 = - \int_{V_1}^{V_2} \frac{T(\partial P / \partial T)_V - P}{C_V} dV.$$

(b) Calculate the temperature change under the Joule process for the ideal gas.

(c) Calculate the temperature change under the Joule process for the van der Waal gas.

a:

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

Joule Process: $\oint Q = 0, \oint W = 0$

$$\delta E = T \delta S - P \delta V = 0 \Leftrightarrow \delta E = 0$$

\Leftrightarrow

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

$$\Leftrightarrow P_s = T \cancel{\delta S} - P$$

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

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

diff
both sides
WRT δV

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

? $\cancel{\frac{\delta T}{\delta E}} \frac{\delta T}{\delta V} = T \left(\frac{\partial P}{\partial T} \right)_V - P$

b.

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

$$PV = NRT$$

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

$\Delta T = 0$ for ideal gas

c.

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

$$\left(P + \frac{\alpha N^2}{V^2} \right) (V - Nb) = NkT \Rightarrow \int_{V_1}^{V_2} \frac{\frac{T N k}{V-nb} - P}{C_V} dV$$

$$\text{Ex } P = \frac{NkT}{V-nb} + \frac{\alpha n^2}{V^2}$$

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

$$\int_{V_1}^{V_2} \frac{\frac{T N k}{C_V} \frac{1}{V-nb} - \frac{P}{C_V}}{C_V} dV$$

$$\left[\frac{TNK}{C_v} \ln |V - nb| - \frac{PV}{C_v} \right] \begin{matrix} V_2 \\ V_1 \end{matrix}$$

$$\left[\frac{TNK}{C_v} \ln |V_L - nb| - \frac{PV_L}{C_v} \right] - \left[\frac{TNK}{C_v} \ln |V_1 - nb| - \frac{PV_1}{C_v} \right]$$

$$\Leftrightarrow \frac{TNK}{C_v} \ln \left| \frac{V_L - nb}{V_1 - nb} \right| - \frac{P}{C_v} (V_L - V_1)$$

$$\Delta T = \frac{TNK}{C_v} \ln \left| \frac{V_L - nb}{V_1 - nb} \right| - \frac{P}{C_v} (V_L - V_1)$$