

Worksheet 2. Solutions

1. Entropy of the ideal gas

consider an ideal gas of Volume V , temperature T and number of particles N .

(1.1) The first law of thermodynamics goes

$$\begin{aligned} dU &= \delta Q + \delta W \\ &= T dS - P dV. \end{aligned} \quad 1.0$$

From the Equipartition theorem

$$U = \frac{3}{2} N k_B T$$

Hence

$$dU = \frac{3}{2} N k_B dT \quad \text{or} \quad N = \text{constant}. \quad (1.1)$$

From the equation of state

$$PV = N k_B T$$

$$P = \frac{N k_B T}{V} \quad (1.2)$$

So replacing 1.1 and 1.2 into 1.0

$$\frac{3}{2} N k_B dT = T dS - \frac{N k_B T}{V} dV$$

Then rearranging terms

$$dS = \frac{3}{2} N k_B \frac{dT}{T} + N k_B \frac{dV}{V} \quad 1.3$$

1.2) Let us integrate eq 1.3 from (T_0, V_0) to (T, V)

$$\int_{S_0}^S dS = \frac{3}{2} N k_B \int_{T_0}^T \frac{dT'}{T'} + N k_B \int_{V_0}^V \frac{dV'}{V'}$$

$$S \Big|_{S_0}^S = S(T, V) - S(T_0, V_0) = \frac{3}{2} N k_B \ln(T) \Big|_{T_0}^T + N k_B (\ln(V')) \Big|_{V_0}^V$$

$$= \frac{3}{2} N k_B \ln \left(\frac{T}{T_0} \right) + N k_B \ln \left(\frac{V}{V_0} \right)$$

$$= N k_B \left\{ \ln \left[\left(\frac{T}{T_0} \right)^{3/2} \right] + \ln \left(\frac{V}{V_0} \right) \right\}$$

$$= N k_B \ln \left[\left(\frac{T}{T_0} \right)^{3/2} \left(\frac{V}{V_0} \right) \right]$$

1.4

finally, as given by the EoS.

$$V = N k_B T / P$$

$$V_0 = N k_B T_0 / P_0$$

$$\frac{V}{V_0} = \frac{T}{T_0} \frac{P_0}{P}$$

1.5

1.3

replacing 1.5 into 1.4

$$\Delta S = S(T, P) - S(T_0, V_0) = N k_B \ln \left[\left(\frac{T}{T_0} \right)^{3/2} \left(\frac{P_0}{P} \right) \right]$$

Note that entropy doesn't have a trivial dependence of the other thermodynamic quantities, still, is an equation of state, and different from the heat, it is an exact differential.

Later, the interpretation of entropy will become clearer and the importance will increase.

Now, we can say

- 1) There is a dependence with the number of particles.
(We consider N fixed, when it is not, the dependence is more complicated)
- 2) Simple dependence with volume (or pressure).
- 3) Dependence with temperature, will change with other ideal gases i.e., diatomic ideal gas.

2. Cycles with non-Ideal gases.

(2.1) The adiabatic curves are defined by $S = \text{constant}$, then we may start from

$$\left. \frac{\partial V(S, T)}{\partial T} \right|_S \quad \text{and using the triple product rule}$$

$$\left(\frac{\partial V}{\partial T} \right) \Big|_S \left(\frac{\partial T}{\partial S} \right) \Big|_V \left(\frac{\partial S}{\partial V} \right) \Big|_T = -1$$

$$\left(\frac{\partial V}{\partial T} \right) = - \left(\frac{\partial S}{\partial T} \right) \Big|_V \frac{1}{(\partial S / \partial V)_T} \quad (2.1)$$

so, taking the Maxwell relation;

$$\left(\frac{\partial S}{\partial V} \right) \Big|_T = \left(\frac{\partial P}{\partial T} \right) \Big|_V \quad (2.2)$$

and

$$C_V = \left(\frac{\partial U}{\partial T} \right) \Big|_V = T \left(\frac{\partial S}{\partial T} \right) \Big|_V \quad (2.3)$$

and replacing (2.3) and (2.2) into (2.1)

$$\left(\frac{\partial V}{\partial T} \right) \Big|_S = -\frac{1}{T} \frac{C_V}{(\partial P / \partial T) \Big|_V} \quad (2.4)$$

2.2.

Taking the equation of state

$$\left(P + \frac{a}{V^2} \right) (V - b) = N k_B T$$

$$P = \frac{N k_B T}{(V - b)} - \frac{a}{V^2}$$

$$\frac{\partial P}{\partial T} = \frac{N k_B}{(V - b)}$$

2.5.

$$C_V = \frac{3}{2} N k_B$$

2.6

So LA Becomes

$$\left(\frac{\partial V}{\partial T} \right)_S = -\frac{1}{T} \frac{3}{2} \cancel{N k_B} \frac{(V - b)}{\cancel{N k_B}}$$

$$= -\frac{3}{2T} (V - b)$$

Then,

$$\frac{dV}{(V - b)} = -3 \frac{dT}{2T}$$

$$\Rightarrow d \ln(V - b) + \frac{3}{2} d \ln(T) = 0$$

$$d \ln \left[(V - b) T^{3/2} \right] = 0$$

$$(V - b) T^{3/2} = \text{const.}$$



$$T = \left(P + \frac{a}{V^2} \right) \frac{(V - b)}{N k_B}$$

$$(V - b)^{5/2} \left(P + \frac{a}{V^2} \right)^{3/2} = \text{cte.}$$

2.3.
Process $1 \rightarrow 2$ isothermal.

$$\Delta U_{12} = \int_{V_1}^{V_2} -P dV = - \int_{V_1}^{V_2} \left(\frac{N k_B T}{V-b} - \frac{a}{V^2} \right) dV$$
$$= - \left[N k_B T_1 \ln(V-b) + \frac{a}{V} \right] \Big|_{V_1}^{V_2}$$
$$= - N k_B T_1 \ln \frac{V_2-b}{V_1-b} - a \left(\frac{1}{V_2} - \frac{1}{V_1} \right)$$

Then

$$\Delta U_{12} = -a \Delta \frac{1}{V} = -a \left(\frac{1}{V_2} - \frac{1}{V_1} \right)$$

Then

$$Q_{12} = \Delta U_{12} - \Delta U_{12} = N k_B T_1 \ln \left(\frac{V_2-b}{V_1-b} \right) < 0$$

$2 \xrightarrow{\text{adiabatic}} 3$

$$Q = 0$$

$$W_{23} = \Delta U = \Delta \left(\frac{3N}{2} T - \frac{a}{V} \right)$$

$$= \frac{3N}{2} (T_3 - T_1) - a \left(\frac{1}{V_2} - \frac{1}{V_3} \right)$$

$3 \xrightarrow{} 4$

The same as $1 \xrightarrow{} 2$, but.

$$V_1 \rightarrow V_3$$

$$V_2 \rightarrow V_4$$

$$T_1 \rightarrow T_3$$

$$W_{34} = -Nk_B T_3 \ln \left(\frac{V_4 - b}{V_3 - b} \right)$$

$$-a \left(\frac{1}{V_4} - \frac{1}{V_3} \right)$$

$$\Delta U_{34} = -a \Delta V$$

$$= -a \left(\frac{1}{V_4} - \frac{1}{V_3} \right)$$

$$Q_{34} = Nk_B T_3 \ln \left(\frac{V_4 - b}{V_3 - b} \right) > 0$$

and $4 \rightarrow 1$ goes like $2 \rightarrow 3$

$$V_2 \rightarrow V_4$$

$$V_3 \rightarrow V_1$$

$$T_1 \leftarrow T_3$$

$$Q_{41} = 0$$

$$W_{41} = \Delta U = \frac{3}{2} N (T_1 - T_3)$$

$$= a \left(\frac{1}{V_1} - \frac{1}{V_4} \right).$$

1.4

Now, we are ready to calculate the efficiency

$$\eta = \frac{W}{Q}$$

The total work

$$W = W_{12} + W_{23} + W_{31} + W_{41},$$

$$= Q_{\text{absorbed}} - Q_{\text{released}}$$

as

$$\oint dU = 0.$$

$$Q_{\text{released}} = N k_B T_3 \ln \left(\frac{V_3 - b}{V_1 - b} \right)$$

$$Q_{\text{absorbed}} = N k_B T_1 \ln \left(\frac{V_1 - b}{V_3 - b} \right)$$

$$\begin{aligned} \eta &= 1 - \frac{Q_{\text{rel}}}{Q_{\text{abs}}} \\ &= 1 - \frac{\cancel{N k_B T_3}}{\cancel{N k_B T_1}} \end{aligned}$$

$$\frac{\ln \left(\frac{V_1 - b}{V_3 - b} \right)}{\ln \left(\frac{V_1 - b}{V_3 - b} \right)}$$

Note that adiabatic curves follow

$$(V_2 - b) T_1^{3/2} = (V_3 - b) T_3^{3/2}$$

Then

$$\frac{V_1 - b}{V_1 - b} = \frac{V_2 - b}{V_3 - b} \propto$$

Hence

$$\begin{aligned}\eta &= 1 - \frac{T_3}{T_1} \\ &\approx 1 - \frac{T_{\text{hot}}}{T_{\text{cold}}}\end{aligned}$$

3. Equation of state.

Let us consider the case in which u depends not only on T .

$$u \stackrel{!}{=} u(T, V).$$

This will imply that $S \stackrel{!}{=} S(T, V)$

So,

$$\begin{aligned} du &= T dS - P dV = T \left. \frac{\partial S}{\partial T} \right|_V dT + T \left. \frac{\partial S}{\partial V} \right|_T dV - P dV \\ &= \underbrace{T \left. \frac{\partial S}{\partial T} \right|_V}_{\frac{\partial u}{\partial T} \Big|_V} dT + \underbrace{\left[T \left. \frac{\partial S}{\partial V} \right|_T - P \right]}_{\frac{\partial u}{\partial V} \Big|_T} dV \end{aligned}$$

and taking the Maxwell relation;

$$\left. \frac{\partial S}{\partial V} \right|_T = \left. \frac{\partial P}{\partial T} \right|_V$$

the equation for the change of internal Energy

$$\left. \frac{\partial u}{\partial V} \right|_T = T \left. \frac{\partial P}{\partial T} \right|_V - P$$

Finally, from the equation of state

$$PV = N k_B T \rightarrow \left. \frac{\partial P}{\partial T} \right|_V = \frac{N k_B}{V}$$

$$T \frac{\partial P}{\partial T} \Big|_V = \frac{N k_B T}{V} = P$$

then

$$\frac{\partial u}{\partial V} \Big|_T = 0 \quad h.$$

therefore $u = u(T)$.

③.1

we have that $u = u(T)$, and

$$\frac{\partial u}{\partial V} \Big|_T = 0 \quad \text{and} \rightarrow T \frac{\partial P}{\partial T} \Big|_V = P$$

integrating

$$\frac{\partial P}{P} = \frac{\partial T}{T}$$

$$\ln(P) = \ln(T) + \ln(f(V))$$

without loss of generality, we can use $\ln(f(V))$ instead of $f(V)$

$$\ln(P) = \ln(f(V)T).$$

$$P = f(V)T \quad h.$$

For the van der Waals gas,

$$\left[P - a \left(\frac{N}{V} \right)^2 \right] \cdot (V - Nb) = Nk_B T.$$

$$P = \frac{Nk_B T}{V - Nb} + a \left(\frac{N}{V} \right)^2$$

We have that

$$C_V = \left. \frac{\partial u}{\partial T} \right|_V$$

and let us study the change of C_V respect to Volume

$$\left. \frac{\partial C_V}{\partial V} \right|_T = \left. \frac{\partial^2 u}{\partial V \partial T} \right|_T$$

$$= \left. \frac{\partial}{\partial T} \left\{ T \left. \frac{\partial P}{\partial T} \right|_V - P \right\} \right|_T$$





$$= \cancel{\left. \frac{\partial T}{\partial T} \right|_V} \cancel{\left. \frac{\partial P}{\partial T} \right|_V} + \left. T \frac{\partial^2 P}{\partial T^2} \right|_V - \cancel{\left. \frac{\partial P}{\partial T} \right|_V}$$

$$= T \left. \frac{\partial^2 P}{\partial T^2} \right|_V = T \frac{\partial}{\partial T} \left(\frac{Nk_B}{V - Nb} \right)$$

$$= 0$$

4. Photon gas Carnot Cycle.

④.1 the work on the cycle is the area in the PV space
in this case approx

$$W = dP dV$$

4.1

④.2 The heat absorbed ^{isotherm.}

$$Q = du + PdV = \left[\frac{\partial u}{\partial T} \Big|_V dT + \frac{\partial u}{\partial V} \Big|_T dV + PdV \right]_T$$

$$= \left[\left(\frac{\partial u}{\partial V} \right)_{\text{isoth}} + P \right] dV$$

4.2

④.3 Then the efficiency $(\eta = \frac{dT}{T})$ from 4.1, 4.2

$$\eta = \frac{W}{Q} = \frac{dP}{\left. \frac{\partial u}{\partial V} \right|_T + P} = \frac{dT}{T}$$

4.3

④.4 from 4.3 and $P = AT^4$

$$T \frac{dP}{dT} = \left. \frac{\partial u}{\partial V} \right|_T + P$$

$$T^4 A T^3 = 4 A T^4 = \left. \frac{\partial u}{\partial V} \right|_T + A T^4$$

$$3 A T^4 = \left. \frac{\partial u}{\partial V} \right|_T$$

integrating

$$U = 3 A T^4 V$$

4.5 an adiabatic path is defined as $Q=0$. and from 1,2

$$Q=0 = \left(\frac{\partial U}{\partial T} \right) \left|_V \right. dT + \left(\frac{\partial U}{\partial V} \right) \left|_T \right. dV + PdV$$

$$\frac{\partial U}{\partial T} = 12AT^3V$$

$$\frac{\partial U}{\partial V} = 3AT^4$$

$$12AT^3VdT + 3AT^4dV + AT^4dV = 0$$

$$12AT^3VdT + 9AT^4dV = 0$$

$$12AT^3VdT + 4PdV = 0$$

$$3V \underbrace{\left(4AT^3dT \right)}_{\frac{dP}{dT} = 4AT^3}$$

$$3VdP + 4PdV = 0$$

$$\frac{dP}{P} = -\frac{4}{3} \frac{dV}{V}$$

$$\ln(P) = -\frac{1}{3} \ln(V) + C$$

$$\ln(P V^{4/3}) = C$$

$$P V^{4/3} = cte.$$