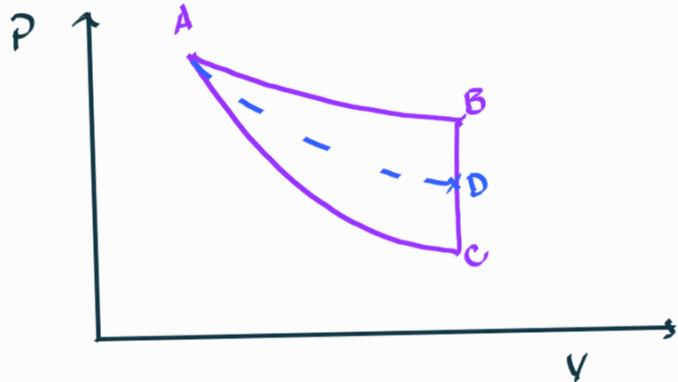


# Worksheet 4. Solutions

## 1. Cycles on ideal gases.

The cycle described is



ii

The transformation AB the gas absorbs an amount of heat

$$Q_{AB} = R T_A \ln \left( \frac{V_B}{V_A} \right) \quad (1)$$

and the heat released during BC

$$Q_{BC} = C_V (T_C - T_B). \quad (2)$$

one of the characteristics of the reversible adiabatic CA

$$T_A V_A^{\gamma-1} = T_C V_C^{\gamma-1} = T_C V_B^{\gamma-1} \quad (3)$$

$$\boxed{\text{as } V_C = V_B.}$$

So, replacing 3 into 1.

$$Q_{AB} = \frac{R T_A}{\gamma-1} \ln \left( \frac{T_A}{T_C} \right) = C_V T_A \ln \left( \frac{T_A}{T_C} \right) \quad (4)$$

so, from ① and ②

$$\begin{aligned} \eta &= 1 + \frac{Q_{BC}}{Q_{AB}} = 1 + \frac{C_V (T_C - T_A)}{C_V T_A \ln \left( \frac{T_A}{T_C} \right)} \\ &= 1 + \left( \frac{T_C}{T_A} - 1 \right) / \ln \left( \frac{T_A}{T_C} \right). \end{aligned}$$

i.e. in the cycle ADCA, we have that.

$$\Delta S_{\text{gas}}^{\text{AD}} + \Delta S_{\text{gas}}^{\text{DC}} = 0$$

and as the only nonreversible transformation AD, the change of the entropy of the universe over all the cycle is the same as  $\Delta S_{\text{gas}}^{\text{AD}}$

$$\Delta S_{\text{gas}}^{\text{DC}} = -\Delta S_{\text{environment}}^{\text{DC}}$$

$$\Delta S_{\text{environment}}^{\text{CA}} = \Delta S_{\text{environment}}^{\text{AD}} = 0$$

$$\Delta S_u = \Delta S_{\text{environment}} = \Delta S_{\text{gas}}^{\text{AD}} = -\Delta S_{\text{gas}}^{\text{DC}} = -C_V \ln \left( \frac{T_c}{T_D} \right)$$

and

$$w = -\Delta U_{AB} - \Delta U_{CA} = C_V (T_c - T_D)$$

2 cycles on diatomic ideal gases.

The cycle considered here goes as

from the reversible adiabatic equation

$$T_A V_A^{\gamma-1} = T_C V_C^{\gamma-1}$$

and from the isobaric

$$\frac{V_C}{V_B} = \frac{T_C}{T_B} = \frac{T_C}{T_A}$$

$$V_C^{\gamma} = V_B V_A^{\gamma-1}$$

$$T_C = \frac{T_A}{V_B} V_C$$

and the efficiency

$$Q_{AB} = n R T_A \ln \left( \frac{V_B}{V_A} \right) < 0$$

$$Q_{BC} = n C_p (T_C - T_B) > 0$$

$$\eta = 1 + \frac{Q_{AB}}{Q_{BC}} = \frac{n R T_A \ln \left( \frac{V_B}{V_A} \right)}{n C_p (T_C - T_B)} + 1.$$

22. The entropy of the universe grows with the only irreversible transformation DA

$$\Delta S_u = \Delta S_{\text{gas}}^{DA} = n C_V \ln \left( \frac{T_A V_A^{\gamma-1}}{T_D V_D^{\gamma-1}} \right)$$

and

$$V_D = \frac{V_A + V_C}{2};$$

$$T_D = \frac{P_D V_D}{n R}$$

$$P_D = P_B = \frac{n R T_B}{V_B} = \frac{n R T_A}{V_B}$$

$$\Delta S_u = C_V \ln \left\{ \frac{T_A}{T_D} \left[ V_A^{\gamma-1} \left[ \frac{2}{V_A + V_C} \right]^{\gamma-1} \right] \right.$$
$$= C_V \ln \left\{ \frac{T_A}{T_D} \left[ \frac{2 V_A}{V_A + V_C} \right]^{\gamma-1} \right\}$$

We have that for a diatomic ideal gas  $\gamma = \frac{7}{5}$

$$\Delta S_u = C_V \ln \left\{ \frac{T_A}{T_D} \left[ \frac{2 V_A}{V_A + V_C} \right]^{\frac{2}{5}} \right\}$$

The condition that must hold so the cycle is possible is

$$\Delta S_u > 0 \rightarrow C_V \ln \left\{ \frac{T_A}{T_D} \left[ \frac{2 V_A}{V_A + V_C} \right]^{\frac{2}{5}} \right\} > 0.$$

### 3 Large and very large numbers.

$$1 \text{ googol} = 10^{100}$$

$$1 \text{ googolplex} = 10^{\text{googol}}$$

1) Which of the properties ( $S$ ,  $T$ ,  $E$  and  $\omega(E)$ ) of our gas sample are larger than a googol? A googleplex?

$T \longrightarrow$  Intensive.

A system doubled in size in thermal equilibrium, remains  $T = \text{constant}$ .

$E, S \longrightarrow$  Extensive.

Energy and entropy depend on the number of particles.

$E$  and  $S \propto N \cdot 10^{23}$  (first order in the number of particles  $\sim N_A$ )

The number of states  $\omega(E) \sim \exp(S/k_B)$

$\sim 10^{(10^{23})} > \text{googol}$

is bigger than a googol, but smaller in scale to a googleplex.

Regarding the units we can use a couple of units to compose

\* human units (daily life units J, m, k).

\* Atomic units (Natural units of  $\hbar$ )

- Human units:

for a mole of material,  $\epsilon, s \propto O(1)$  in the units. Therefore, the previous analysis holds.

- Atomic units

for refining the measurement of the volume in the phase space in units of  $\hbar^{3N}$ , it make sense as

$$\sqrt{(2m\pi E)}^{3/2} < 1$$

The volume gets smaller as  $N$  increases.  
→ Units are important.

3.2

it is clear that

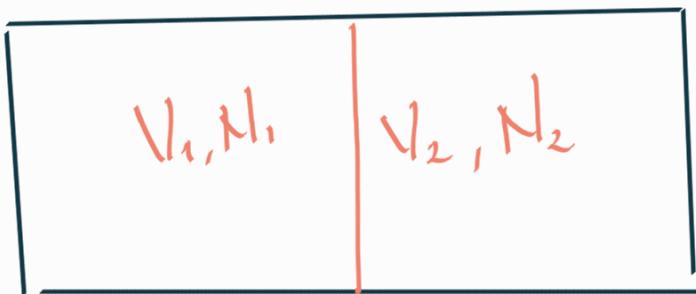
T intensive

S, E extensive

$\omega$  foster.

4 Microstates in a Simple System.

Consider



$V, N$

we know that the total number of states goes as

$$\begin{aligned}\Omega_{\text{tot}}(N, V) &\propto V^N \\ &= (V_1 + V_2)^N \\ &= \sum_{N_1=0}^N \binom{N}{N_1} V_1^{N_1} V_2^{N-N_1}\end{aligned}$$

and using that

$$N_2 = N - N_1$$

and

$$\Omega_1(N_1, V_1) \propto V_1^{N_1}, \quad \Omega_2(N_2, V_2) \propto V_2^{N_2}$$

as the term  $\binom{N}{N_1}$  accounts the number of repetitions compatible with the configuration, a particular value  $k$  for  $N_1$  leads to;

$$\Omega(V_1, N_1, k, N) = \binom{N}{k} V_1^k V_2^{N-k}$$

Therefore, the probability of having  $k$  particles in  $V_1$ ,

$$P_k = \frac{\Omega(V_1, N_1, k, N)}{\Omega_{\text{Tot}}(V, N)} = \frac{\binom{N}{k} V_1^k V_2^{N-k}}{\sum_{N_1=0}^N \binom{N}{N_1} V_1^{N_1} V_2^{N-N_1}}$$

$$= \binom{N}{k} (PV)^k (qV)^{N-k}$$


 $\frac{1}{V^N}$ 
 $\rightarrow \Omega_{\text{Tot}} \propto V^N$

$$= \binom{N}{k} p^k q^{N-k}$$

~~$\frac{(N-k)! k!}{N!}$~~ 
 $\cancel{V^N}$

$$= \left(\frac{N}{k}\right) p^k q^{N-k}$$

Such that, the average

$$\bar{k} = \sum_{k=0}^N P_k k$$

$$= \sum_{k=0}^N \binom{N}{k} k p^k q^{N-k}$$

and using  $x p^x = p \frac{\partial}{\partial p} (p^x)$

$$\bar{k} = \sum_{k=0}^N \binom{N}{k} q^{N-k} p \frac{\partial}{\partial p} p^k$$

$$= p \frac{\partial}{\partial p} \left[ \sum_{k=0}^N \binom{N}{k} q^{N-k} p^k \right]$$

and using again the binomial theorem

$$\bar{k} = p \frac{\partial}{\partial p} (p+q)^N = N p \cancel{(p+q)^{N+1}} \quad p+q=1$$

$$= N p.$$

$$\frac{\bar{k}}{N} = p = \frac{1}{V}$$

4.5)  $\overline{(\Delta k)^2} = \sum_{k=0}^N p_k (k - \bar{k})^2 = \sum_{k=0}^N p_k (k^2 + \bar{k}^2 - 2k\bar{k})$

$$= \sum_{k=0}^N p_k k^2 + \bar{k}^2 \sum_{k=0}^N p_k - 2\bar{k} \sum_{k=0}^N p_k k$$

$$= \sum_{k=0}^N p_k k^2 + \bar{k}^2$$

and recursively

$$k^2 p^k = \left( p \frac{\partial}{\partial p} \right)^2 p^k$$

$$\overline{(\Delta k)^2} = \left( p \frac{\partial}{\partial p} \right)^2 (p+q)^N - (pN)^2$$

$$= p \left[ N(p+q)^{N-1} + pN(N-1)(p+q)^{N-2} \right] - (pN)^2$$

$$= pN + p^2 N(N-1) - (pN)^2$$

~~$$= pN + (pN)^2 - p^2 N - (pN)^2$$~~

$$= pN - p^2 N = p(1-p)N = pqN$$

$$\Delta^* k = \sqrt{(\Delta k)^2} \propto \sqrt{N}$$

## 5 Free Energy + Enthalpy

The internal energy for an ideal gas:

$$U(S, V, N) = U_0 \left( \frac{N}{N_0} \right)^{5/3} \left( \frac{V_0}{V} \right)^{2/3} \exp \left\{ \frac{2}{3} \left( \frac{S}{Nk_B} - s_0 \right) \right\}$$

and the Helmholtz free energy

$$F = U - TS$$

To obtain the free energy  $F \equiv F(T, V, N)$ , then we need to change the dependence on  $U(S)$ .

$$\frac{\partial F}{\partial S} = 0 = \frac{\partial U}{\partial S} - T \frac{\partial S}{\partial S}$$

$$\Rightarrow T = \frac{\partial U}{\partial S} = U(S, V, N) \frac{2}{3} \frac{1}{Nk_B}$$

$$\frac{3}{2} Nk_B T U_0^{-1} \left( \frac{N_0}{N} \right)^{5/3} \left( \frac{V}{V_0} \right)^{2/3} = \exp \left[ \frac{2}{3} \left( \frac{S}{Nk_B} - s_0 \right) \right]$$

$$\frac{3}{2} \ln \left[ \frac{3}{2} Nk_B T U_0^{-1} \left( \frac{N_0}{N} \right)^{5/3} \left( \frac{V}{V_0} \right)^{2/3} \right] = \frac{S}{Nk_B} - s_0$$

$$S = Nk_B \left\{ s_0 + \ln \left[ \left( \frac{3}{2} \frac{Nk_B T}{U_0} \right)^{3/2} \left( \frac{N_0}{N} \right)^{5/2} \left( \frac{V}{V_0} \right) \right] \right\}$$

if we take  $U_0 = \frac{3}{2} N_0 k_B T_0$  — Eq. theorem.

$$F(T, V, N) = Nk_B T \left\{ \frac{3}{2} - s_0 - \ln \left[ \left( \frac{T}{T_0} \right)^{3/2} \left( \frac{N_0}{N} \right) \left( \frac{V}{V_0} \right) \right] \right\}$$

The entropy and internal energy are equations of state.  
Let us study F. To do so, compute the derivatives.

Let us call

$$\eta = \left(\frac{T}{T_0}\right)^{3/2} \left(\frac{N_0}{N}\right) \left(\frac{V}{V_0}\right)$$

$$= T^{3/2} \left(\frac{1}{T_0}\right)^{3/2} \left(\frac{N_0}{N}\right) \left(\frac{V}{V_0}\right)$$

$$\frac{\partial F}{\partial T} = N k_B \left[ \frac{3}{2} - S_0 - \ln(\eta) \right] - N k_B T \left[ \frac{\partial}{\partial T} \ln(\eta) \right]$$

$$\frac{\partial}{\partial T} \ln(\eta) = \frac{1}{\eta} \frac{\partial \eta}{\partial T} = \frac{1}{\eta} \left[ \frac{3}{2} \frac{1}{T} \chi \right]$$

$$= -N k_B \left[ S_0 + \ln(\eta) \right]$$

$$-\frac{\partial F}{\partial T} = N k_B \left\{ S_0 + \ln \left[ \left(\frac{T}{T_0}\right)^{3/2} \left(\frac{N_0}{N}\right) \left(\frac{V}{V_0}\right) \right] \right\} = S(T, V, N)$$

$$\frac{\partial F}{\partial V} = -N k_B T \frac{\partial}{\partial V} \ln(\eta)$$

$$= -N k_B T \frac{1}{\eta} \frac{\partial \eta}{\partial V}$$

$$= -N k_B T \frac{1}{\eta} = -\frac{N k_B T}{V} = -P$$

$$P = -\frac{\partial F}{\partial V}$$

Even, one can calculate the chemical potential

$$\mu = \frac{\partial F}{\partial N} = k_B T \left\{ \frac{S}{2} - S_0 - \ln \left[ \left( \frac{T}{T_0} \right)^{3/2} \left( \frac{N_0}{N} \right) \left( \frac{V}{V_0} \right) \right] \right\}$$

one can calculate

$$F(T, V, N) + TS = \frac{S}{2} N k_B T = U(T, V, N). \quad \text{L.}$$

the two of them are equivalent.

5.3) Let us start with the definition of the enthalpy

$$H = U + PV$$

and as

$$-P = \frac{\partial U}{\partial V} = -\frac{2}{3} U_0 \left( \frac{N}{N_0} \right)^{5/3} \frac{V_0^{2/3}}{V^{5/3}} \exp \left( \frac{2}{3} \left( \frac{S}{N k_B} - S_0 \right) \right)$$

and from here, getting the volume as.

$$\left(\frac{V}{V_0}\right)^{5/3} = \frac{2}{3} U_0 \left(\frac{N}{N_0}\right)^{5/3} p \frac{1}{V_0} \exp\left(\frac{2}{3}\left(\frac{S}{Nk_B} - s_0\right)\right)$$
$$\frac{V}{V_0} = \left(\frac{N}{N_0}\right) \left(\frac{2}{3} \frac{U_0}{pV_0}\right)^{3/5} \exp\left[\frac{2}{5}\left(\frac{S}{Nk_B} - s_0\right)\right]$$

The enthalpy leads

$$H = U_0 \left(\frac{N}{N_0}\right)^{5/3} \left(\frac{V_0}{V}\right)^{2/3} \exp\left\{\frac{2}{3}\left(\frac{S}{Nk_B} - s_0\right)\right\}$$
$$+ p V_0 \left(\frac{2}{3} \frac{U_0}{pV_0}\right)^{3/5} \left(\frac{N}{N_0}\right) \exp\left\{\frac{2}{5}\left(\frac{S}{Nk_B} - s_0\right)\right\}$$

let us work on the first term

$$U = U_0 \left(\frac{N}{N_0}\right)^{5/3} \left(\frac{V_0}{V}\right)^{2/3} \exp\left(\frac{2}{3}\left(\frac{S}{Nk_B} - s_0\right)\right)$$
$$= U_0 \left(\frac{N}{N_0}\right) \exp\left(\frac{2}{5}\left(\frac{S}{Nk_B} - s_0\right)\right)$$
$$\times \left(\frac{N}{N_0} \frac{V_0}{V}\right)^{2/3} \exp\left[\frac{5}{3}\left(\frac{S}{Nk_B} - s_0\right)\right]$$
$$= U_0 \left(\frac{N}{N_0}\right) \exp\left(\frac{2}{5}\left(\frac{S}{Nk_B} - s_0\right)\right)$$
$$\times \left\{ \left(\frac{N}{N_0} \frac{V_0}{V}\right)^{5/3} \exp\left[\frac{2}{3}\left(\frac{S}{Nk_B} - s_0\right)\right] \right\}^{2/5}$$

$$\frac{3}{2} \frac{pV_0}{U_0}$$

$$U = U_0 \left( \frac{N}{N_0} \right) \left( \frac{3}{2} \frac{U_0}{PV_0} \right)^{-2/5} \exp \left( \frac{2}{5} \left( \frac{S}{k_B N} - s_0 \right) \right)$$

Then, the enthalpy

$$H(S, p, N) = \exp \left\{ \frac{2}{5} \left( \frac{S}{k_B N} - s_0 \right) \right\} \left( \frac{N}{N_0} \right) \times \underbrace{\left[ U_0 \left( \frac{2}{3} \frac{U_0}{PV_0} \right)^{-2/5} + PV_0 \left( \frac{2}{3} \frac{U_0}{PV_0} \right)^{3/5} \right]}_{\text{the last term}}$$

$$\begin{aligned} U_0 \left( \frac{3}{2} \frac{U_0}{PV_0} \right)^{-2/5} + PV_0 \left( \frac{2}{3} \frac{U_0}{PV_0} \right)^{3/5} &= \left( \frac{3}{2} \frac{U_0}{PV_0} \right)^{-2/5} \left( U_0 + PV_0 \left( \frac{2}{3} \frac{U_0}{PV_0} \right) \right) \\ &= \left( \frac{3}{2} \frac{U_0}{PV_0} \right)^{-2/5} \left( U_0 + \frac{2}{3} U_0 \right) \\ &= \frac{5}{3} U_0 \left( \frac{3}{2} \frac{U_0}{PV_0} \right)^{-2/5} \end{aligned}$$

lastly

$$H(S, p, N) = \frac{5}{3} U_0 \left( \frac{3}{2} \frac{U_0}{PV_0} \right)^{-2/5} \left( \frac{N}{N_0} \right) \exp \left\{ \frac{2}{5} \left( \frac{S}{k_B N} - s_0 \right) \right\}$$

if we take  $U_0 = \frac{3}{2} N_0 k_B T_0 = \frac{3}{2} P_0 V_0$

$$H(S, p, N) = \frac{5}{3} U_0 \left( \frac{N}{N_0} \right) \left( \frac{P}{P_0} \right)^{2/5} \exp \left\{ \frac{2}{5} \left( \frac{S}{k_B N} - s_0 \right) \right\}$$

6. Free energy  
Let us take the work done by an expansion from  $V_0$  to  $V$

$$w = 2 V_0 \log \left( \frac{V}{V_0} \right)$$

and the entropy

$$S = R \frac{V_0}{V} \cdot \left( \frac{T}{T_0} \right)^a$$

1 Helmholtz free energy

Let us use the Maxwell relations;

$$-S = \left. \frac{\partial F}{\partial T} \right|_V$$

and

$$-P = \left. \frac{\partial F}{\partial V} \right|_T$$

Let us calculate  $F(V, T_0)$  integrating over an isotherm.

$$\cancel{dF = -SdT - PdV} = -P \int_{V_0}^V dV = -w$$

$$\Delta F = F(V, T_0) + F(T) = -R V_0 \log \left( \frac{V}{V_0} \right)$$

and second, integrating S over an isochoric.

$$F(V, T) = - \int_{T_0}^T S dT + F(V)$$

$$= - \int_{T_0}^T R \frac{V_0}{V} \frac{1}{T_0^a} T^a dT + F(V)$$

$$= -R \frac{V_0}{V} \left[ \frac{\frac{T^{a+1}}{a+1} - \frac{1}{T_0^a}}{\frac{1}{T_0^a}} \right]_{T_0}^T + F(V)$$

$$= -R \frac{V_0}{V} \frac{\frac{T^{a+1}}{a+1} - \frac{T_0^{a+1}}{a+1}}{\frac{T_0^{a+1}}{a+1}} T_0 + F(V)$$

$$= -\frac{RV_0T_0}{(a+1)V} \left[ \left( \frac{T}{T_0} \right)^{a+1} - 1 \right] + F(V)$$

Then

$$F(V, T) = -\frac{RV_0T_0}{(a+1)V} \left[ \left( \frac{T}{T_0} \right)^{a+1} - 1 \right] - R V_0 \log \left( \frac{V}{V_0} \right)$$

2, the equation of state.

from the Maxwell equation used before;

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

$$= \frac{RV_0}{V(a+1)} \left( \frac{T}{T_0} \right)^a$$

$$PV = RV_0 \left( \frac{T}{T_0} \right)^a$$

3. Let us use the work over the isotherm. T

$$\begin{aligned} W &= \int P dV \\ &= \int_{V_0}^V P dV \\ &= \int_{V_0}^{V'} R V_0 \left(\frac{T}{T_0}\right)^{\alpha} dV' \\ &= \int_{V_0}^V \frac{R V_0}{V'} \left(\frac{T}{T_0}\right)^{\alpha} dV' \\ &= R V_0 \left(\frac{T}{T_0}\right)^{\alpha} \int_{V_0}^V \frac{dV'}{V'} \\ &= R V_0 \left(\frac{T}{T_0}\right)^{\alpha} \log\left(\frac{V}{V_0}\right) \end{aligned}$$