Weds: Faculty candidates

Thurs: Read 2.14, 2.16, 2.21

Fri: HW 5pm

Chemical potential

We can consider systems which interact and whose particle number is variable. The maximum entropy principle implies that, when these are in equilibrium with each other the quantity

$$\left(\frac{\partial S}{\partial N}\right)_{E,V}$$

is the same for each. We thus define:

> The chemical potential of a system is
> $$\mu := -T\left(\frac{\partial S}{\partial N}\right)_{E,V}$$

This immediately implies that

> Two systems that exchange particles will be in equilibrium
> $\Rightarrow$ chemical potentials of the systems are equal.

Thus chemical potential is analogous to temperature but deals with particle number.

Now consider two interacting systems whose volumes are fixed. Then

$$dS = dS_A + dS_B$$

$$= \left(\frac{\partial S_A}{\partial E_A}\right)_{V_A, N_A} dE_A + \left(\frac{\partial S_A}{\partial V_A}\right)_{E_A, N_A} d\!\!\!/V_A^{\;\;0} + \left(\frac{\partial S_A}{\partial N_A}\right)_{E_A, V_A} dN_A$$

$$+ \text{ similar for } B$$

$$= \frac{1}{T_A} dE_A - \frac{\mu_A}{T_A} dN_A + \frac{1}{T_B} dE_B - \frac{\mu_B}{T_B} dN_B.$$

Suppose the total energy and total particle numbers are fixed. Then:

$$dS = \left(\frac{1}{T_A} - \frac{1}{T_B}\right) dE_A - \left(\frac{\mu_A}{T_A} - \frac{\mu_B}{T_B}\right) dN_A$$

Consider an instant at which the temperatures are the same. So $T_A = T_B = T$. Then

$$dS = -\frac{1}{T}(\mu_A - \mu_B) dN_A$$

We require $dS \geqslant 0$

$$\Rightarrow -\frac{1}{T}(\mu_A - \mu_B) dN_A \geqslant 0 \qquad \Rightarrow -(\mu_A - \mu_B) dN_A \geqslant 0.$$

So if $\mu_A > \mu_B$ then $dN_A \leqslant 0$.

if $\mu_A < \mu_B$ then $dN_A \geqslant 0$

The system with lower chemical potential gains particles from the system with higher chemical potential.

Fundamental thermodynamic identity

We have

$$dS = \left(\frac{\partial S}{\partial E}\right)_{V,N} dE + \left(\frac{\partial S}{\partial V}\right)_{E,N} dV + \left(\frac{\partial S}{\partial N}\right)_{E,V} dN$$

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

$=0$

$$\boxed{dE = TdS - PdV + \mu dN}$$

This identity has many roles. First $TdS = \delta Q$ also gives

$$dE = \delta Q - PdV + \mu dN$$

Then:

1) It allows us to <u>determine energy changes</u>

$$\Delta E = \underbrace{\int \delta Q}_{\text{heat}} - \underbrace{\int PdV}_{\substack{\text{work on} \\ \text{gas}}} + \underbrace{\int \mu dN}_{\substack{\text{energy added by} \\ \text{additional particles}}}$$

So the chemical potential also quantifies the energy cost associated with more particles.

2) It relates many thermodynamic quantities via derivatives and calculus. So

$$dE = \left(\frac{\partial E}{\partial S}\right)_{V,N} dS + \left(\frac{\partial E}{\partial V}\right)_{S,N} dV + \left(\frac{\partial E}{\partial N}\right)_{S,V} dN$$

$\Rightarrow \quad T = \left(\frac{\partial E}{\partial S}\right)_{V,N} \qquad -P = \left(\frac{\partial E}{\partial V}\right)_{S,N} \qquad$ etc,...

1 Fundamental Thermodynamic Identity

a) Rewrite the fundamental thermodynamic identity in the form

$$dS = \ldots$$

b) Us the previous results plus standard calculus of differentials to express various thermodynamic quantities in terms of derivatives of entropy.

Answer:

a)
$$dE = TdS - PdV + \mu dN$$

$$\Rightarrow \quad TdS = dE + PdV - \mu dN$$

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

b) If we regard S as a function of E, V, N, then:

$$dS = \left(\frac{\partial S}{\partial E}\right)_{V,N} dE + \left(\frac{\partial S}{\partial V}\right)_{E,N} dV + \left(\frac{\partial S}{\partial N}\right)_{E,V} dN$$

Comparing expressions gives:

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N} \qquad \Rightarrow \qquad T = 1 \Big/ \left(\frac{\partial S}{\partial E}\right)_{V,N}$$

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{E,N} \qquad \Rightarrow \qquad P = T \left(\frac{\partial S}{\partial V}\right)_{E,N}$$

$$\frac{-\mu}{T} = \left(\frac{\partial S}{\partial N}\right)_{E,V} \qquad \Rightarrow \qquad \mu = -T \left(\frac{\partial S}{\partial N}\right)_{E,V}$$

Entropy for an ideal gas

The entropy for any system depends only on the state of the system. We would like to find the entropy of an ideal gas as a function of state variables: T, P, V, N. Thus we seek

$$S = S(T, V, N)$$

since the pressure equation of state can reexpress this in terms of say pressure. We start with:

Relationships from fundamental thermodynamic identity	Energy and pressure equations of state
$$\left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{1}{T}$$	$$PV = NkT$$
$$\left(\frac{\partial S}{\partial V}\right)_{E,N} = \frac{P}{T}$$	$$E = fNkT = fPV$$ $$f = \tfrac{3}{2}, \tfrac{5}{2}, \dots$$
$$\left(\frac{\partial S}{\partial N}\right)_{E,V} = -\frac{\mu}{T}$$	

Then the right sides of the above need to be expressed as functions of E, V, N. To this end

$$E = fNkT \implies T = \frac{E}{fNk} \implies \left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{fNk}{E}$$

$$P/T = \frac{Nk}{V} \implies \qquad \dots \implies \left(\frac{\partial S}{\partial V}\right)_{E,N} = \frac{Nk}{V}$$

$$\dots \implies \left(\frac{\partial S}{\partial N}\right)_{E,V} = -\frac{fNk}{E}\mu$$

We could now attempt to solve these. However, μ could depend on temperature or energy or volume. We do not yet know this dependence for an ideal gas. So we cannot determine entropy completely. We will be able to determine it as a function of T, V but not N. To do so

$$\left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{fNk}{E} \quad \Rightarrow \quad \int \left(\frac{\partial S}{\partial E}\right)_{V,N} dE = \int \frac{fNk}{E} dE$$

$$\Rightarrow \quad S = fNk \ln(E) + g(V,N)$$

Now

$$\left(\frac{\partial S}{\partial V}\right)_{E,N} = \frac{Nk}{V} \quad \Rightarrow \quad \left(\frac{\partial g}{\partial V}\right)_N = \frac{Nk}{V}$$

$$\Rightarrow \quad \underbrace{\int \left(\frac{\partial g}{\partial V}\right)_N dV}_{g(V,N)} = \int \frac{Nk}{V} dV = Nk \ln V + h(N)$$

$\nearrow$ unknown function of N

Thus $\quad g(V,N) = Nk \ln(V) + h(N)$. So

$$S = fNk \ln(E) + Nk \ln(V) + h(N)$$

$$= fNk \ln(fNkT) + Nk \ln(V) + h(N)$$

$$= fNk \left[\ln(fNk) + \ln(T)\right] + Nk \ln(V) + h(N)$$

$$= fNk \ln(T) + Nk \ln(V) + \tilde{h}(N)$$

So

For an ideal gas

$$S(T,V,N) = fNk \ln(T) + Nk \ln(V) + \tilde{h}(N)$$

where $f = \frac{3}{2}$ (monoatomic), $\frac{5}{2}$ (diatomic),... and $\tilde{h}(N)$ is an unknown function.

Heat Engines

A heat engine is a device that converts heat into useful work.

DEMO :* PSU - 5   (Now YouTube)
     * Otto cycle

Such engines consist of a working material / thermodynamic system whose primary purpose is to effect the conversion of heat into work. The working material can be any thermodynamic system but we will focus on a gas. The requirements will be:

1) the engine will undergo a series of quasistatic processes

2) the engine must be reusable and so must return to the same state at some point.

Thus the engine will repeatedly cycle through the same process and.

> The state of the working material at the end of the cycle must be the same as at the beginning of the cycle.

We will analyze the engine over a single cycle. For example consider the Otto cycle:

Stage	V	P	T	ΔE	W	Q	
① Intake	-	-	-	-	-	-	
② adiabatic	↓	↑	↑	+ve	+ve	O	piston does work on gas
③ const vol/ignition	const	↑	↑	+ve	O	+ve	supply heat COST
④ adiabatic	↑	↓	↓	-ve	+ve	O	gas does work on piston
⑤ const vol	const	↓	↓	-ve	O	-ve	lose heat ≡ WASTE
⑥ expel waste gas	-	-	-	-	-	-	
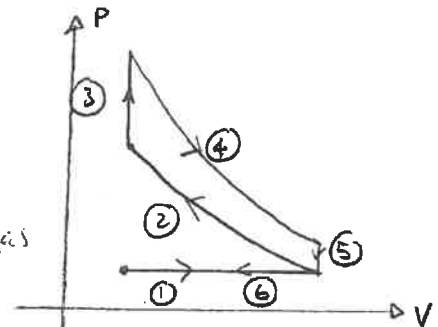
The efficiency of the engine can be analyzed on a per-cycle basis. We aim to compare:

1) the net work over the entire cycle, subtracting work done on the gas whenever it occurs.

2) the heat supplied which constitutes the cost. This excludes the heat leaving the gas which is regarded as waste.

Then the thermal efficiency of the engine is:

$$\eta := \frac{\text{work done in one cycle}}{\text{heat supplied in one cycle.}}$$

Note that this ignores the heat ejected in one cycle. Then it will emerge that the two laws of thermodynamics can answer:

1) for a given cycle what is the efficiency

2) is there an engine for which the efficiency is 1?

3) if not what is the optimal efficiency?

2 Heat engine

A cylinder contains 0.040 mol of a monoatomic ideal gas, which undergoes the process indicated on the PV diagram. The curved line is an isothermal expansion.

a) Determine the work done, change in energy and heat entering or leaving the gas in each stage.

b) Determine the change in energy over the entire cycle.

c) Determine the thermal efficiency of the engine.

d) Determine maximum and minimum temperature of the gas during the cycle.

P in 10^5 Pa

V in $10^{-3}\,\text{m}^3$

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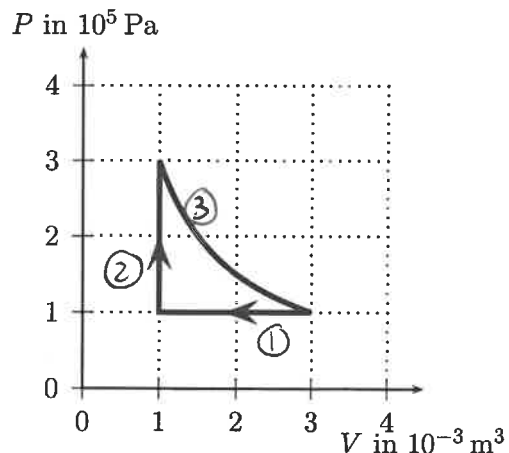
a) * Work done is $\qquad W = -\int PdV$

* For a monoatomic ideal gas

$$E = \tfrac{3}{2}PV \qquad \Rightarrow \qquad \Delta E = \tfrac{3}{2}\Delta(PV)$$

* First law $\Rightarrow \qquad Q = \Delta E - W$

Stage ①
$$W = -\int PdV = -\text{ area under PV}$$
$$= -\left(-10^5 P_a\right) \times 2.0\times 10^3\,\text{m}^3 = 200\text{J}.$$

$$\Delta E = \tfrac{3}{2}\Delta(PV) = \tfrac{3}{2}\left(P_f V_f - P_i V_i\right) = \tfrac{3}{2}\left(100\text{J} - 300\text{ J}\right) = -300\text{J}$$

$$Q = -300\text{J} - 200\text{J} \qquad = -500\text{J}.$$

Stage 2
$$W = 0 \qquad \text{since } V = \text{const}$$
$$\Delta E = \tfrac{3}{2}\left(P_f V_f - P_i V_i\right) = \tfrac{3}{2}\left(300\text{J} - 100\text{J}\right) = 300\text{J}$$
$$Q = 300\text{J} - W = 300\text{J}$$

Stage 3 $W = -\int P\,dV$

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

$$W = -NkT \int_{V_i}^{V_f} \frac{dV}{V}$$

$$= -NkT \ln(V_f/V_i)$$

$$= -NkT \ln(3)$$

Now along the curve T is constant. So $NkT = P_i V_i$ at start

$$= 300J.$$

$$\Rightarrow W = -300J \ln 3$$

Since T is constant, E is constant $\Rightarrow \Delta E = 0$, finally

$$Q = \Delta E - W = 330J$$

Stage	W	ΔE	Q
①	200J	-300J	-500J
②	0J	300J	300J
③	-330J	0	330J
loop			0J

b) Adding gives $\Delta E = 0$

c) Heat is supplied in stages ②,③. So

   heat supplied $= 630J$

   The total work done on the gas is $200J - 330J = -130J$

   Thus the gas does work $130J$

$$\Rightarrow \quad \eta = \frac{130J}{630J} = 0.21$$

d) The temperature is given by $T = \frac{PV}{Nk}$ and is largest when PV is largest.

Along the isotherm $PV = 300J$

$$N = 0.040 \times 6.02 \times 10^{23} = 2.4 \times 10^{22}$$

and

$$T = \frac{300J}{2.4 \times 10^{22} \times 1.38 \times 10^{-23} J/k}$$

$$= 900K$$

Minimum temperature is at the bottom. $PV = NkT \Rightarrow 100J = NkT$

$$\Rightarrow \quad T = 300K.$$

We can analyze the efficiency of the process in terms of heat flows. In order for heat to

a) enter in stage ③, the system must be in contact with an environment at temp $> 900K$.

b) leave in stages ①, the system must be in contact with an environment at temp $< 300K$.

We can envisage the engine as operating between two reservoirs. Then let:

high temp
(at least 900K)

↓ heat enters Q_{high}
does work W
on surroundings
↓ heat leaves Q_{low}

low temp
(at most 300K)

$Q_{high} = |$ heat entering system in one cycle $|$

$Q_{low} = |$ heat leaving system in one cycle $|$

$W_{out} = $ work done by gas in one cycle.
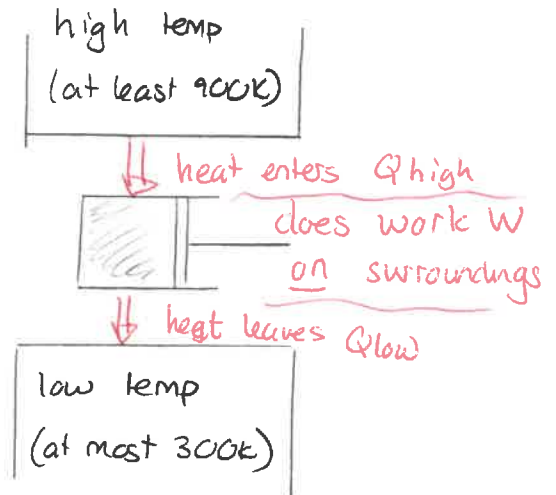
So

$$\eta = \frac{W_{out}}{Q_{high}}$$

Now the first law gives

$$\Delta E = Q_{high} - Q_{low} - W_{out}$$

For a cycle $\Delta E = 0 \implies W_{out} = Q_{high} - Q_{low}$

Thus

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

Clearly $Q_{low} \leq Q_{high}$. So $\eta \leq 1$. What is the best that we can do between those two baths?