Chapter 10 The Mechanical Interaction

Recall: $dE = dQ - dW + \mu\, dN$

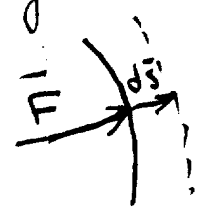
focus of this chapter

A. Change in Volume

From the fundamental definition of work:

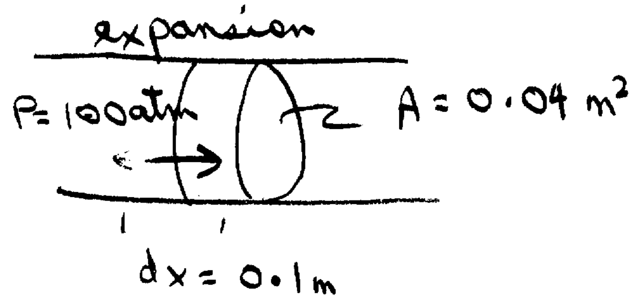
$dW = \underline{F} \cdot d\underline{s}$

force, displacement



$= P \times A \times ds = \underline{\underline{P\, dV}}$

Example



$W = ?$

$W = \int dW = \int P\, dx = P\, \Delta x$

P = constant ∴ can bring outside the $\int$

$= 100 \cancel{atm} \times 10^5 \frac{Pa}{\cancel{atm}} \times (0.04 \times 0.1)\, m^3$

$= 10^7 \times 4 \times 10^{-3}\ \frac{N}{m^2} \cdot m^3$

$= 4 \times 10^{+4}$ N-m

$= 4 \times 10^4$ J done by the system

Example

In the prev. example, assume gas had 10^{28} molecules with $\nu = 5$ d.o.f.

What is ΔT ?

$$dE = \cancel{dQ}^{0} - dW + \cancel{\mu\, dN}_{0} = -(+4 \times 10^{4}\,J)$$

$$= \tfrac{1}{2} \mathcal{R} k\, dT \qquad \mathcal{R} = 5 \times 10^{28}$$

$$(\text{since } E = \tfrac{1}{2} \mathcal{R} k T) \qquad k = 1.381 \times 10^{-23}\, J/K$$

$$\therefore\ dT = \frac{-4 \times 10^{4}\,J}{\tfrac{1}{2} \times 5 \times 10^{28} \times 1.381 \times 10^{-23}} = -0.11\ K$$

B. Work and the Number of Accessible States

We had the 1st Law: $dE = dQ - dW + \mu dN$

$dQ = TdS$ since $\left.\frac{\partial S}{\partial E}\right)_{V,N} = \frac{1}{T}$, $dW = PdV$

ie $dE = TdS - PdV + \mu dN$ —— ①

7 variables: E, T, S, P, V, μ, N

\# independent variables = # of types of interactions

= thermal, mechanical, diffusive

= 3

Can pick any 3, ie

$E = E(T, S, P)$

$T = T(P, \mu, N)$ etc.

⋮

It makes sense to express energy in terms of exact differentials dS, dV, dN

The other variables T, P + μ are measurable + are given by:

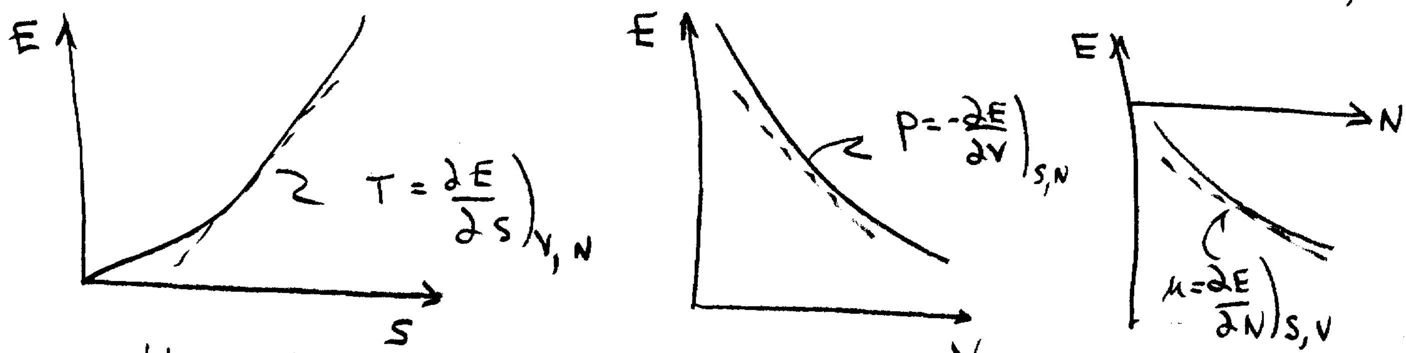
$$T = \left.\frac{\partial E}{\partial S}\right)_{V,N}, \quad P = -\left.\frac{\partial E}{\partial V}\right)_{S,N}, \quad \mu = \left.\frac{\partial E}{\partial N}\right)_{S,V}$$

(from ① above)

We can also rearrange ①!

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

$$\text{\&}\quad \frac{1}{T} = \left.\frac{\partial S}{\partial E}\right)_{V,N}, \quad \frac{P}{T} = \left.\frac{\partial S}{\partial V}\right)_{E,N}, \quad \frac{\mu}{T} = -\left.\frac{\partial S}{\partial N}\right)_{E,N}$$



thermal only   mech. only   diff. only

In this chapter we focus on

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

Recall $S = k \ln \Omega \implies P = kT \left.\frac{\partial \ln \Omega}{\partial V}\right)_{E,N}$

$$\therefore \frac{P\Delta V}{kT} = \Delta \ln \Omega = \ln \Omega_2 - \ln \Omega_1$$

$$= \ln\left(\frac{\Omega_2}{\Omega_1}\right)$$

ie $\dfrac{\Omega_2}{\Omega_1} = e^{P\Delta V/kT}$

This is really $\dfrac{\Omega_2}{\Omega_1} = e^{\Delta Q/kT}$ that we saw before (9-10 my notes, eq. 15 in text)

(ie $\Delta E = \Delta Q - P\Delta V + \mu \Delta N$ at const $E, N \Rightarrow \Delta Q = P\Delta V$)

So Pressure = measure of how S↑ or Ω ↑ as V↑.

<u>Example</u>

$20\,m^3$ of air at room T & P

↘ expands by 0.001%

What is $\frac{\Omega_2}{\Omega_1}$? Assume E & N const.

$$\frac{\Omega_2}{\Omega_1} = e^{P\Delta V/kT}$$

$$= e^{\frac{(10^5\, N/m^2)(10^{-5} \times 20\, m^3)}{1.381 \times 10^{-23} J/K \times 300 K}}$$

$$= e^{4.8 \times 10^{21}} = 10^{2.1 \times 10^{21}}$$

We have seen ~~that~~ Ω ↑ rapidly as E ↑.

Here we see ~~that~~ Ω ↑ " " V ↑.

So it should be no surprise to find (next chapter) ~~that~~ Ω ↑ rapidly as N ↑.

C. Other Kinds of Works

We can generalize:

$$dE = T\,dS - dW + \mu\,dN$$

$$F\,ds \Rightarrow \sum_i \mathcal{F}_i\,dx_i$$

where $\mathcal{F}_i\,dx_i$ are different kinds of force & displacement.

Examples:

dx	$\mathcal{F}$	dW
Position	Mechanical	$F_x\,dx$
Volume	Pressure	$p\,dV$
Elect. potential	charge	$-q\,dU$
Magnetic	moment	$\mu\,dB$
Separation	Gravity	$-\dfrac{Gm_1m_2}{r^2}\,dr$

not same as diffusive potential μ.

Example

System (closed) with $q = +10^{-12}$ C.

What is ΔS when U decreased by 1 V?

(potential)

$T = 300$ K = const.

Soln:

$dW = -q\,dU$ ← replaces dV

(q replaces P)

We had $\frac{P}{T} = \left.\frac{\partial S}{\partial V}\right)_{E,N} \Rightarrow \frac{q}{T} = \left.\frac{\partial S}{\partial U}\right)_{E,N}$

$\therefore \Delta S = -\frac{q}{T}\,\Delta U = \frac{10^{-12}}{300} \times 1 \quad \left(\frac{C \cdot V}{K}\right)$ ← J/K

$= 3.3 \times 10^{-15}$ J/K

Example:

What is $\frac{\Omega_2}{\Omega_1}$ in the above?

$$\frac{\Omega_2}{\Omega_1} = e^{\Delta W/kT} = e^{-q\Delta U/kT} = e^{\Delta S/k}$$

recall $\Delta S = k \ln\left(\frac{\Omega_2}{\Omega_1}\right)$

$$= e^{\frac{3.3 \times 10^{-15}\ J/K}{1.381 \times 10^{-23}\ J/K}}$$

$$= e^{2.4 \times 10^{8}} = 10^{1.1 \times 10^{8}}$$

D. Thermal Expansion and Compressibilities

Most materials expand when heated

Define

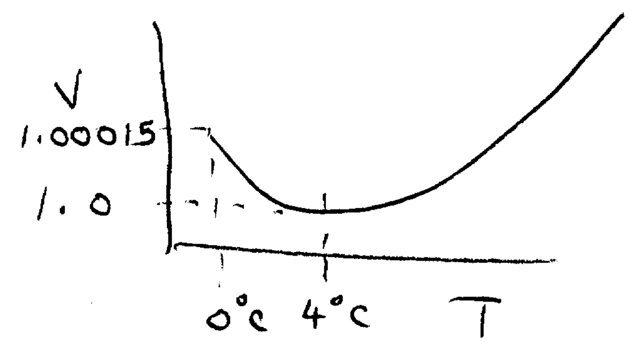
β = coefficient of volume expansion $\equiv \frac{1}{V}\left.\frac{\partial V}{\partial T}\right)_P$

Typically $\beta = \beta(T,P)$, $\beta > 0$

For small changes: $\Delta V = \left.\frac{\partial V}{\partial T}\right)_P \Delta T = V\beta\,\Delta T$

2nd order effects → 0

H_2O is an exception



Without this, life as we know it wouldn't exist.

see Stowe P 170 for some β's for various substances

Also have

α = coeff. of linear expansion $= \frac{1}{X}\left.\frac{\partial X}{\partial T}\right)_P$ ← length

$\Delta X = \left.\frac{\partial x}{\partial T}\right)_P \Delta T = X\alpha\,\Delta T$

Since $V' = V + \Delta V = (X+\Delta X)(y+\Delta y)(z+\Delta z)$ ← assuming α is the same in all 3 directions

$= X(1+\alpha\Delta T)\,Y(1+\alpha\Delta T)\,Z(1+\alpha\Delta T)$

$= V(1+\alpha\Delta T)^3 \simeq V(1+3\alpha\Delta T)$

we ~~see that~~ $\boxed{\beta = 3\alpha.}$

We also have

$$\kappa = \text{isothermal compressibility} \equiv -\frac{1}{V}\frac{\partial V}{\partial P}\Big)_T$$

As before

$$\kappa = \kappa(T, P)$$

$$\Delta V = -V\kappa\,\Delta P$$

$$\frac{1}{\kappa} \equiv \text{bulk modulus} = -V\frac{\partial P}{\partial V}\Big)_T$$