

Chapter 14 Imposed Constraints

A. The Reduction of Independent Variables

$dN = 0$ Nondiffusive

$dV = 0$ Isovolumic or isochoric

$dQ = 0$ Adiabatic

$dP = 0$ Isobaric

$dT = 0$ Isothermal

When we study a process, we want to use these constraints in our formulation.

To help you in setting your solution up, ask:

1. What property do we wish to study?
2. What are the constraints
3. What properties can we most easily measure?

In general we want to use:

$$\Delta W = \left. \frac{\partial W}{\partial x} \right|_{y,z} \Delta x + \left. \frac{\partial W}{\partial y} \right|_{x,z} \Delta y + \left. \frac{\partial W}{\partial z} \right|_{x,y} \Delta z$$

Example

How does E vary when we heat a beaker of water?

We have: $dN=0$, $dP=0$

We want dE

$$dE(N, P, S) = \left. \frac{\partial E}{\partial N} \right|_{P, S} dN + \left. \frac{\partial E}{\partial P} \right|_{N, S} dP + \left. \frac{\partial E}{\partial S} \right|_{N, P} dS$$

constrained

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

①

But what is this? This doesn't appear in Maxwell's list.

∴ go back to basics:

We have $dE(S, V, N) = Tds - pdv + \mu dN$ — ②

$$dV = \left. \frac{\partial V}{\partial S} \right|_{P, N} dS + \left. \frac{\partial V}{\partial P} \right|_{S, N} dP + \left. \frac{\partial V}{\partial N} \right|_{S, P} dN$$

$f_N(S, P, N)$

$$= \left. \frac{\partial V}{\partial S} \right|_{P, N} dS$$

Subst into ② $\Rightarrow dE = Tds - p \left. \frac{\partial V}{\partial S} \right|_{P, N} dS$

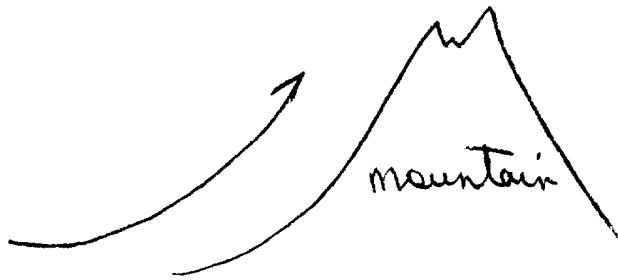
$$= \left(T - p \left. \frac{\partial V}{\partial S} \right|_{P, N} \right) dS$$

$\uparrow \frac{dQ}{T}$

Aside: Why bother?

$$dE(Q, V, N) = dQ - p dV + \mu dN$$

(= $C_V dT$)

Example

How does T vary with elevation?

Assume air mass stays intact + no energy is transferred. P varies

$$dN = 0, dS = 0$$

$$dT(P, S, N) = \left. \frac{\partial T}{\partial P} \right|_{S, N} dP + \left. \frac{\partial T}{\partial S} \right|_{P, N} dS + \left. \frac{\partial T}{\partial N} \right|_{S, P} dN$$

B. Isobaric Processes

Constant P , eg outer space, deep ocean, open atmosphere

$$\text{Can use } dH = Tds + v dp + \mu dN$$

$$\left. \begin{array}{l} \\ \\ \end{array} \right\} = Tds \quad \text{if } dN = 0$$

heat function

Ideal gas law is simple at const. P ;

$$pV = NkT \Rightarrow \frac{V}{T} = \text{const.}$$

But for solids & liquids, need measurements;

$$\beta = \left. \frac{1}{v} \frac{\partial v}{\partial T} \right|_p$$

& we find that $\beta = f_n(T, P)$, ie \neq const.

C. Isothermal Processes

Sometimes use $dF = -SdT - p dV + \mu dN$

Work function $\int^A = -p dV$ if $dN = 0$

example: microorganisms in the ocean.

$$pV = RT = \text{const.} \quad \leftarrow \text{gas}$$

$$K = -\frac{1}{V} \left. \frac{\partial V}{\partial p} \right|_T \quad \leftarrow \text{solids + liquids}$$

D. Adiabatic Processes

$$dQ = 0$$

Eg: compression of gas in a car engine
($\sim 0.02s$ - too fast for heat transfer)

Eg: massive deep ocean currents.

If $dN = 0$ as well, we only have 1 variable.

D.1 Adiabatic Processes in Gases

$$\begin{aligned} \text{We have } dE &= dQ - pdV + \mu dN \quad \text{set } = 0 \\ &= -pdV \end{aligned} \quad \text{--- (1)}$$

$$\text{Also } E = \frac{\nu}{2} NKT \Rightarrow dE = \frac{\nu}{2} NK dT \quad \text{--- (2)}$$

$$\text{Ideal gas: } PV = NKT \Rightarrow pdV + vdp = NK dT \quad \text{--- (3)}$$

3 eqn's & 4 differentials: dE, dT, dP, dV
We can rearrange them.

$$\text{(1) + (2)} \Rightarrow \frac{\nu}{2} NK dT = -pdV$$

$$\text{sub into (3)} \Rightarrow pdV + vdp = \frac{-2p}{\nu} dV$$

$$\Rightarrow \left(\frac{\nu+2}{\nu}\right) pdV + vdp = 0$$

$$\Rightarrow \left(\frac{\nu+2}{\nu}\right) \frac{dV}{V} + \frac{dP}{P} = 0$$

$$\gamma \equiv \frac{\nu+2}{\nu}$$

$$\Rightarrow \left(\frac{\nu+2}{\nu}\right) \ln V + \ln P = \text{const}$$

$$\Rightarrow \boxed{PV^\gamma = \text{const}}$$

Adiabatic compression
& expansion

Also, since $PV = NKT$

$$PV^\gamma = (PV) V^{\gamma-1} = \text{const}$$

$$= NKT V^{\gamma-1} = \text{const}$$

$$\therefore \boxed{TV^{\gamma-1} = \text{const.}}$$

We can relate γ to C as follows:

1st Law: $dE = dQ - pdV + \mu dN$

$$\Rightarrow dQ = dE + pdV$$

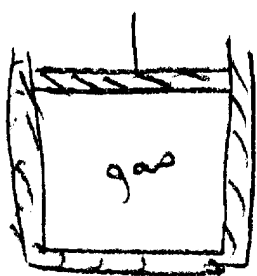
$$\therefore \left. \frac{\partial Q}{\partial T} \right|_V = \left. \frac{\partial E}{\partial T} \right|_V = C_V = \frac{\nu}{2} NK$$

$$\left. \frac{\partial Q}{\partial T} \right|_P = \left. \frac{\partial E}{\partial T} \right|_P + \underbrace{p \left. \frac{\partial V}{\partial T} \right|_P}_{= NK} = C_P$$

$$\uparrow = \frac{\nu}{2} NK$$

$$\therefore \frac{C_P}{C_V} = \frac{(\frac{\nu}{2} + 1) NK}{\frac{\nu}{2} NK} = \frac{\nu + 2}{\nu} = \gamma$$

Can easily find γ experimentally:



move piston $P_1 V_1^\gamma = P_2 V_2^\gamma$

measure P_1, V_1
 P_2, V_2

$$\Rightarrow \left(\frac{V_1}{V_2} \right)^\gamma = \frac{P_2}{P_1}$$

$$\gamma \ln(V_1/V_2) = \ln P_2/P_1$$

$$\therefore \gamma = \frac{\ln P_2/P_1}{\ln V_1/V_2}$$

(Additional material - not in Stowe)

14-7a

What happens to S in an adiabatic ($dQ=0$) expansion at equilibrium?

$$dS = \frac{dQ}{T} \quad \therefore dS = 0$$

$$\begin{aligned} - \text{But } dE &= dQ - PdV + \mu dN \quad (\text{assume } dN=0) \\ &= -PdV \neq 0 \end{aligned}$$

$$dV > 0 \quad \therefore dE < 0$$

$$- \text{And } S = k \ln \Omega, \quad \Omega = \text{const } E^{R/2}$$

$$\therefore \text{if } E \downarrow, \Omega \downarrow \therefore S \downarrow$$

But above we said $dS=0$!!!

How come?

Because Ω is a function of other things as well as E .

$$\text{Recall that } \Omega = \text{const } E^{R/2}$$

↑ can't write E

Ω is a function of E but it is also a function of other system variables, such as volume, i.e.

$$\Omega = \text{const}' V^N E^{R/2} \quad \text{for instance.}$$

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

↑ $\frac{1}{T} \Leftarrow$ defined at equilibrium \Leftarrow Note

$$\therefore dS = \frac{1}{T} \left(dE + \underbrace{T \left(\frac{\partial S}{\partial V} \right)_{E,N}}_P dV + \underbrace{T \left(\frac{\partial S}{\partial N} \right)_{V,E}}_{-\mu} dN \right)$$

$$= \frac{dQ}{T}$$

D.2 Adiabatic Processes in Liquids & Solids

For liquids & solids we don't have anything like the ideal gas law to help us. We rely on Maxwell's relations & set $ds=0$, $dN=0$ to simplify.

For systems at \equiv^m & adiabatic ($dQ=0$) $\Rightarrow ds=0$

$$T, V \text{ chosen as variables} \quad ds = \left. \frac{\partial S}{\partial T} \right|_V dT + \left. \frac{\partial S}{\partial V} \right|_T dV = 0 \quad \text{--- ①}$$

$$T, P \text{ chosen as variables} \quad ds = \left. \frac{\partial S}{\partial T} \right|_P dT + \left. \frac{\partial S}{\partial P} \right|_T dP = 0 \quad \text{--- ②}$$

Now, we had $\left. \frac{\partial S}{\partial T} \right|_V = \frac{C_V}{T}$, $\left. \frac{\partial S}{\partial T} \right|_P = \frac{C_P}{T}$

And Maxwell's relations give us:

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

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

from $dV = \left. \frac{\partial V}{\partial P} \right|_T dP + \left. \frac{\partial V}{\partial T} \right|_P dT$
 $= -V\kappa dP + V\beta dT$
 $dP = \frac{\beta}{\kappa} dT - \frac{1}{V\kappa} dV$

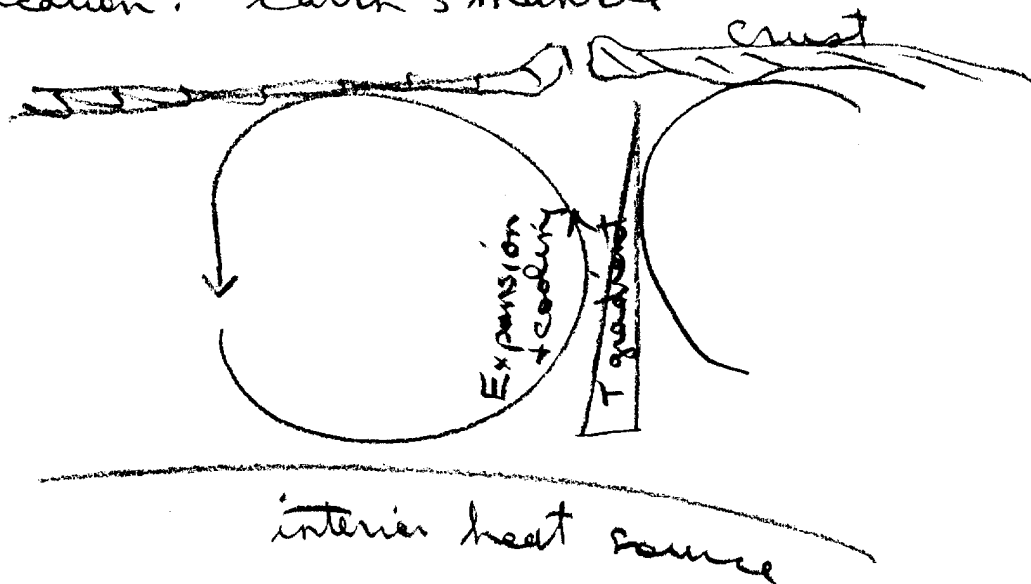
Thus ① $\Rightarrow ds = \frac{C_V}{T} dT + \frac{\beta}{\kappa} dV = 0 \Rightarrow \boxed{\frac{dT}{T} = -\frac{\beta}{\kappa C_V} dV}$

② $\Rightarrow ds = \frac{C_P}{T} dT - V\beta dP = 0 \Rightarrow \boxed{\frac{dT}{T} = \frac{V\beta}{C_P} dP}$

These apply to
adiabatic, $dN=0$
systems
at \equiv^m .

$$\boxed{\frac{dV}{V} = -\frac{\kappa C_V}{C_P} dP}$$

Application: Earth's mantle



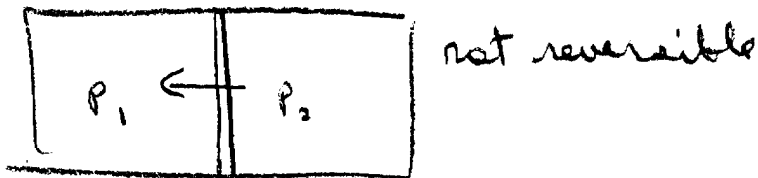
As mantle heats & rises, $P \downarrow \therefore V \uparrow + T \downarrow$

IF $T \downarrow$ due to adiabatic expansion is $<$ T drop due to conduction & convection, then mantle rises. Otherwise it sinks.

E. Reversibility

We know that $\Delta S_0 \geq 0$ (2nd Law)

\therefore a reversible process (back to original state) must be one in which $\Delta S_0 = 0$, because can't have $\Delta S_0 < 0$ at any time.



$$P_2 > P_1$$



$$T_2 > T_1$$

- Interacting systems must be at \cong^m at all times if it is to be reversible (i.e. $\Delta S = 0$)
- Friction causes increased random motion, $\therefore S \uparrow \therefore$ irreversible.

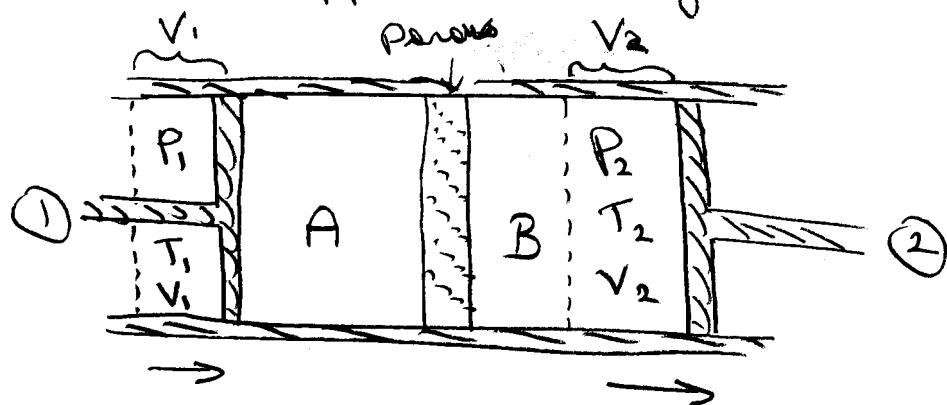
Quasi-static means a slow process - systems stay in \cong^m .

F. Nonequilibrium Process

- Thermodynamics is about Ξ^m processes usually.
- non- Ξ^m is much more difficult since we don't have the general statistical tools.
- However, there are some important non- Ξ^m processes which we will look at.

F.1 Joule-Thompson (Throttling) Process

What happens to the gas as it expands?



✓ prefer this explanation than that in stems

We push on 1 & pull on 2 so that gas is pushed through the porous plug. Pressure in region A is maintained at P_1 , Pressure in region B is maintained at P_2

$\Delta E = E_2 - E_1 =$ change in energy of the volume that is moved.

$$= -P \Delta V \text{ for area A (work is done on A)}$$

$$-P \Delta V \text{ for area B (work is done by B)}$$

$$= P_1 V_1 - P_2 V_2$$

$$\therefore E_2 + P_2 V_2 = H_2 = E_1 + P_1 V_1 = H_1$$

$$\therefore H = \text{constant} \Rightarrow dH = 0$$

This is an irreversible process.

Joule-Thompson coefficient $\equiv \mu \equiv \left(\frac{\partial T}{\partial P} \right)_H$

μ depends on properties of gas.

Typically $\mu < 0$. $\mu = 0$ for ideal gas.

Now we can write, holding N constant:

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP = 0$$

i.e. $H = H(T, P)$

ie, these 2 processes cancel out.

$$\therefore dT = - \frac{\left(\frac{\partial H}{\partial P}\right)_T dP}{\left(\frac{\partial H}{\partial T}\right)_P}$$

We evaluate these as follows:

$$H = E + PV \Rightarrow dH = dE + PdV + VdP$$

$$\therefore dH = dQ - PdV + PdV + VdP = dQ + VdP$$

(N constant)

$$\therefore \left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial Q}{\partial T}\right)_P = C_p$$

$$\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial Q}{\partial P}\right)_T + V$$

$$= T \left(\frac{\partial S}{\partial P}\right)_T + V = -V\beta T + V = V(1 - \beta T)$$

$$\therefore dT = - \frac{V(1 - \beta T)}{C_p} dP$$

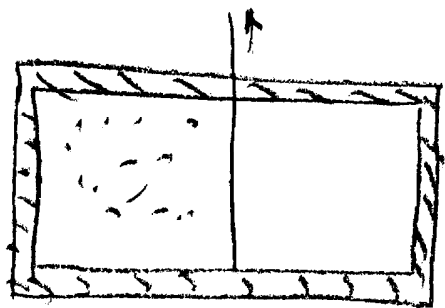
$$\beta \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P$$

Note: Here we are evaluating $\left(\frac{\partial H}{\partial P}\right)_T + \left(\frac{\partial H}{\partial T}\right)_P$ in general. P & T are not constant in the throttling process.

Ideal gas: $PV = nRT \Rightarrow V = \frac{nRT}{P} \Rightarrow \left(\frac{1}{V} \frac{\partial V}{\partial T}\right)_P = \frac{nR}{VP} = \frac{1}{T}$

$$\therefore \text{for ideal gas: } dT = - \frac{V(1 - \frac{T}{T})}{C_p} dP = 0$$

F.2 Free Expansion of a Gas

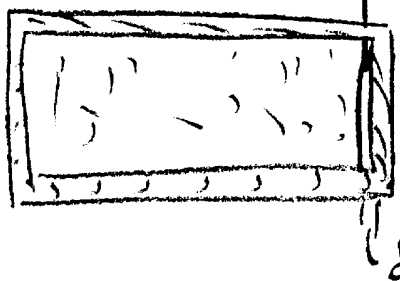


Remove barrier.

$$\Delta E = \Delta Q - \Delta W = 0$$

\uparrow_0 \uparrow_0

For an infinitesimal change



$$dE = 0 = Tds - pdv$$

$$\therefore ds = \frac{p}{T} dv$$

We want to relate $T+V$, not $S+V$ so:

$$dS = \left. \frac{\partial S}{\partial T} \right|_V dT + \left. \frac{\partial S}{\partial V} \right|_T dV$$

$$\uparrow \frac{1}{T} C_V$$

$$\left. \frac{\partial p}{\partial T} \right|_V$$

$$\therefore \frac{1}{T} C_V dT + \left. \frac{\partial p}{\partial T} \right|_V dV = \frac{p}{T} dV$$

$$\therefore dT = \frac{1}{C_V} \left[p - T \left. \frac{\partial p}{\partial T} \right|_V \right] dV$$

(Problem 14-19)

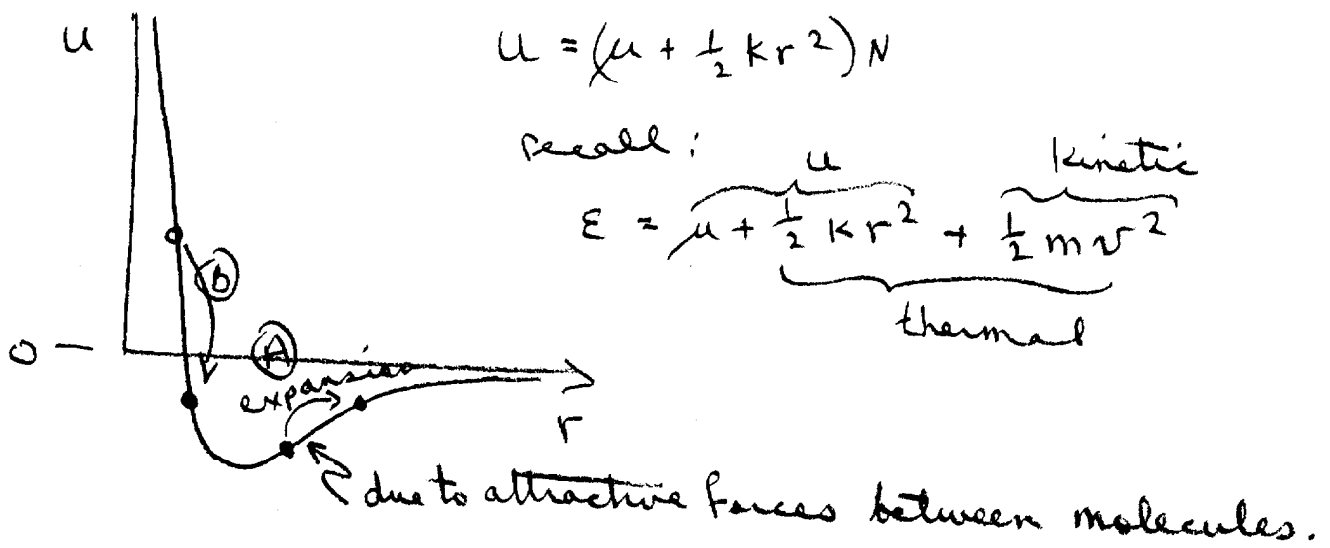
dT for ideal gas?

$$PV = nRT \Rightarrow T \left. \frac{\partial p}{\partial T} \right|_V = p$$

$$\therefore dT = 0$$

get this from the gas law
(ideal or van der Waals,
as appropriate)

Will $T \uparrow$ or \downarrow when $V \uparrow$? Can tell by looking at potential well!



(A) $\Delta E = 0 + U \uparrow$ when $V \uparrow \therefore K.E. \downarrow \therefore T \downarrow$

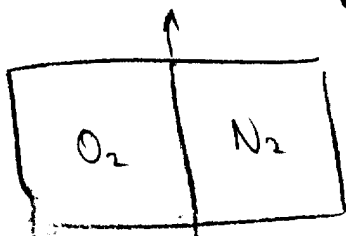
(B) $\Delta E = 0 + U \downarrow$ " $V \downarrow \therefore T \uparrow$

So expect most gases to cool upon expansion.

But if gas is highly compressed, it will heat up upon expansion.

\therefore highly compressed H_2 gas is explosive!

F.3 Removal of Barrier Constraints



Removal of barrier between distinguishable gases causes $S \uparrow$ even if at same $P, T, \text{ etc.}$

\therefore Irreversible