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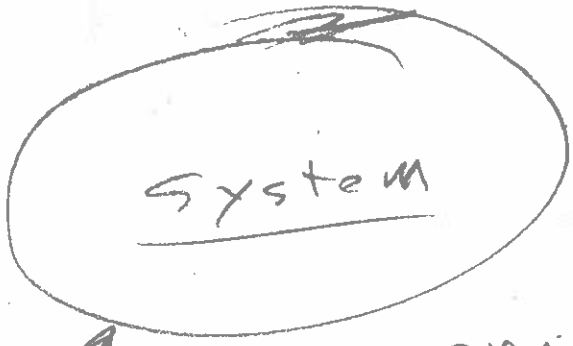
Ch 20 1st Law of Thermodynamics

20.1) Thermodynamic Systems and Equation of State

a) A physical system is that part of the universe to break of to study in detail.



boundary

environment

A thermodynamic system is the special case where you are studying its thermodynamics

The environment is the rest of the universe.

You are only interest in the environment insofar as it effects the system

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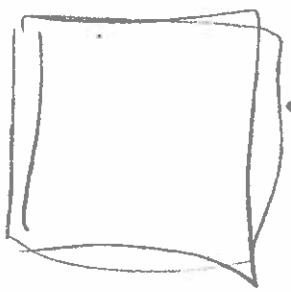
The boundary is between,
It's usually a spatial boundary, but it doesn't have to be.

A closed system is completely unaffected by the environment and we often invoke those in thermodynamics.

An open system is affected by the environment,

Thermodynamic closed system



← Thermal isolated, volume constant

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We are mostly going to consider systems that have uniform intensive thermodynamic variable values: eg,

uniform temperature,
uniform density,
uniform internal energy density,
uniform entropy density,
uniform substance, uniform phase, etc,

And usually we just consider thermodynamic equilibrium (TE) states

and quasistatic processes

The system changes its state slowly enough that it can be regarded as passing through a

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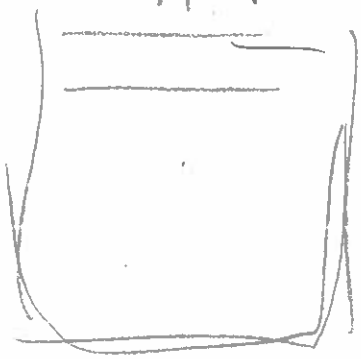
Example open system

← Thermal contact but constant volume

or



← Thermal isolated but the piston can change volume and do work on the system,

In thermodynamics jargon, this PdV work (P–d–V work)

= Pressure Volume Work

continuum of TE states (20005)
and you do NOT need
to consider non-TE states,

A quasistatic process is an
ideal limit, but many
actual processes approximate
quasistatic processes very well.
And even when NOT,
quasistatic processes
allow understanding.

b) Equation of State (EOS)

An equation of state is a
relationship among
the independent variables
of a thermodynamic system
in thermodynamic equilibrium.
All other variables can be calculated
from the independent ones.

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For example

$$f(P, V, T) = 0$$

pressure, volume, temperature

3 independent variables.

But actually there may be implicit ones you consider constant

$$f(P, V, T, M, \text{Composition}) = 0$$

mass composition

If these are allowed to change, they can't be left implicit

Composition can change if you inject or remove species

But also if you allow e.g., chemical or nuclear reactions.

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You also have choice about which variables you choose to be your independent variables

For examples,

a) $f(P, V, T, M) = 0$

can be replaced by

$f(P, \rho, T, M) = 0$

$\rho = \frac{M}{V}$ is density

b) $f(P, V, S, M) = 0$

Entropy It is more obscure than temperature, but it can be more useful if actually

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Know its relationships to other variables which often involves statistical (mechanics (microscopic thermodynamics)

c) $f(E, V, T) = 0$

internal energy (extensive, Not density)

Often you would like equation of state written as a function

pressure $P = f(V, T)$

internal energy $E = f(V, T)$

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All-important example
of an equation
of state
(the prototype
in fact)
is the ideal gas law

$$PV = NkT$$

P: Pressure
V: volume
N: number of particles
T: kelvin temperature

or $P = nkT$

n: density of particles

But you can also write its
EOS in terms
of internal energy

$$E = \frac{d}{2} NkT$$

but alas $d = d(T, P)$ in general

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So even ideal gases get more complex if you go beyond monatomic gases

Also the ideal gas law does contain entropy and statistical mechanics calculation needs to be done to find a formula for entropy (which we are NOT going to do)

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20.3 1st Law of Thermodynamics

(Energy conservation in the context of thermodynamics)

a) A general form is differential form. (see Ling-118)

$$dE = \delta Q - \delta W$$

(Were keeping mass and composition fixed)

E is internal energy of the system

Q is heat added – if negative then heat is removed

Work done by the system

If negative, work transfers energy to the system

Writing with explicit minus sign is to allow us to think of work done by the system rather than work done on the system. It's just the convention for work

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The δ in
δQ and δW
mean not exact
or integral differentials.

There is NO
function $Q(T, P, \ldots)$
or $W(T, P, \ldots)$,

δQ and δW are just
amounts.

This version of 1st
is NOT restricted
to the system
being in thermodynamic
equilibrium (TE)

And it has its uses,
but non-TE states
are harder analyze,
and so we skirt
them.

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b) 1st Law for system in TE undergoing Quasistatic Processes

A rather general Version

$$dE = TdS - PdV + \sum_i \mu_i dN_i$$

exact differentials. They can be integrated for finite change.

internal energy as function of entropy, volume, composition

$$E(S, V, \{N_i\})$$

entropy, volume, composition

temperature $$T = \left(\frac{\partial E}{\partial S}\right)_{V, N_i}$$

$$\mu_i = \left(\frac{\partial E}{\partial N_i}\right)_{S, V, \text{other } N_i}$$

pressure $$P = -\left(\frac{\partial E}{\partial V}\right)_{S, N_i}$$

Variables held constant when the partial derivative is taken

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We are NOT going to delve into chemical potentials, but they are necessary if the necessary if species change by reactions (chemical or nuclear) or particles are actually being added or removed.

So dropping chemical potential (Not allowing composition change or mass added/subtracted from system)

c) We have the simplest form of 1st Law

$$dE = TdS - PdV$$

TdS: heat added to the system at constant temperature

PdV: Work done by system at constant pressure

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When I say constant T and constant P, I mean relative to the differential expression

Say you knew

$T(S,V)$ | $P(S,V)$

$$\Delta E_{1,2} = \int_{S_1}^{S_2} T(S,V)\,dS$$

change in internal energy due to change in entropy at constant volume

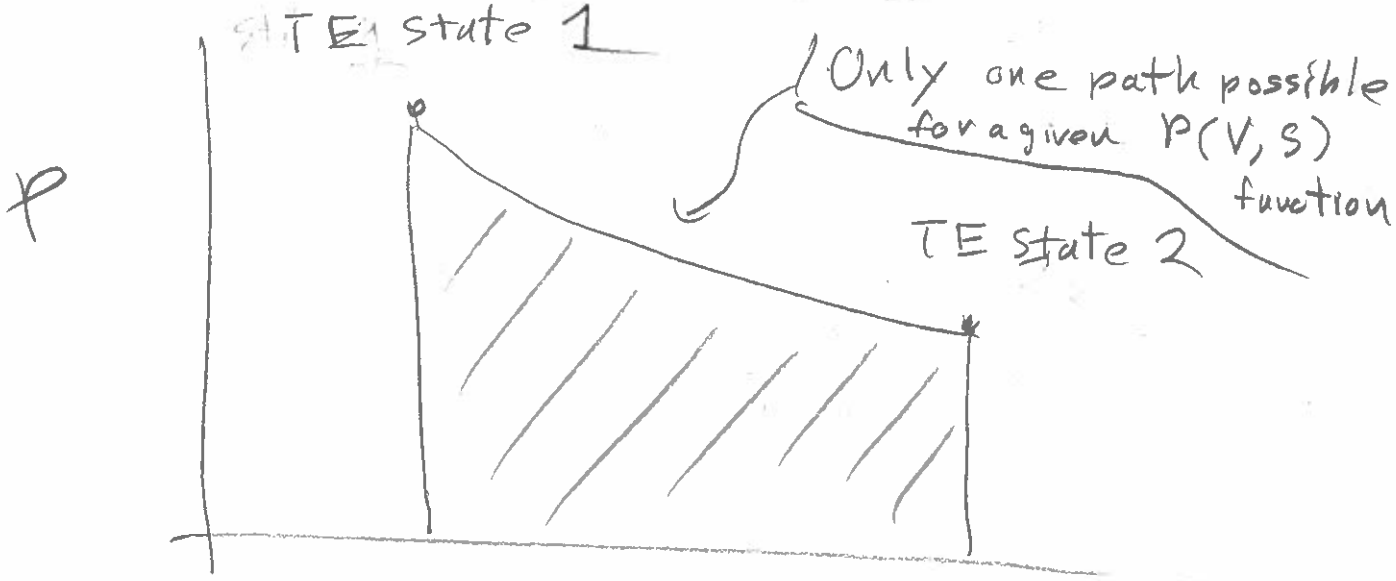
$$\Delta E_{12} = -\int_{V_1}^{V_2} P(S,V)\,d$$

change in internal energy at constant entropy due change in volume

No change in entropy is an adiabatic change (or No heat flow)

20016 d) Illustration

on a PV diagram (Wiki)



$$\Delta E = -\int_1^2 P(V,s)\,dV = -W_{done}$$

$$= -\text{Area under curve}$$

Positive in PV diagram

$\therefore \Delta E < 0$

Internal energy was lost and went into Work.

Macroscopic Work.

The system could be gas pushing a piston.

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What if you went from State 1 to State 2

No heat flows

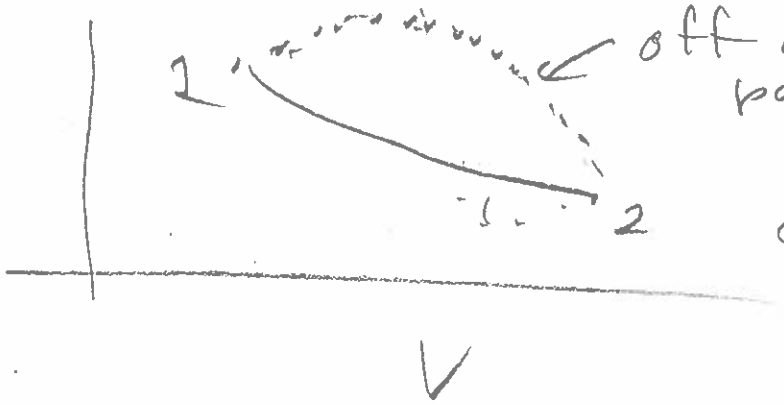
adiabatically, but NOT quasistatically.

so endpoints in $\mathbb{E}$ but not in between.

$\Delta \mathbb{E}_{12}$ must still be the same and No heat flowed

$\therefore$ $W_{done} = -\Delta \mathbb{E}_{12}$

↳ is still the same



off diagram path. P, T, ρ could be change wildly and be non uniform

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The adiabatic quasistatic process allowed you to calculate the work done even though the in between states may be very non-TE and often hard or impossible to calculate.

To generalize, quasistatic process calculations can tell you about cumulative amounts of change for processes that are NOT quasistatic.

So. quasistatic process calculations can be a useful in analyzing things like heat engines which seldom quasostatic

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e) An Isothermal Process for an ideal Gas

For an ideal gas in the case of fixed number of degrees of freedom and equipartition of energy

(Ling-81) $E = \frac{d}{2} NkT$

$= \frac{d}{2} n_{mol} RT$

(Ling-73) $P = \frac{n_{mol} RT}{V}$

We don't have $E = E(S, V)$ or $P = P(S, V)$, and so an adiabatic work calculation can't be done but we can do an isothermal calculation; i.e. constant temperature

$dW = -PdV$ is still valid

It's just work done by our macroscopic definition.

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$$W = \int_{V_1}^{V_2} \frac{n_{mol} R T}{V} \, dV$$

(with T constant)

$$= n_{mol} R T \ln\left(\frac{V_2}{V_1}\right)$$

If $V_2 / V_1 > 1$,

positive work done

and $\Delta E_{work} = -W < 0$,

but $E = \frac{d}{2} n_{mol} R T$

is unchange; i.e. $\Delta E = 0$

No dependence on T.

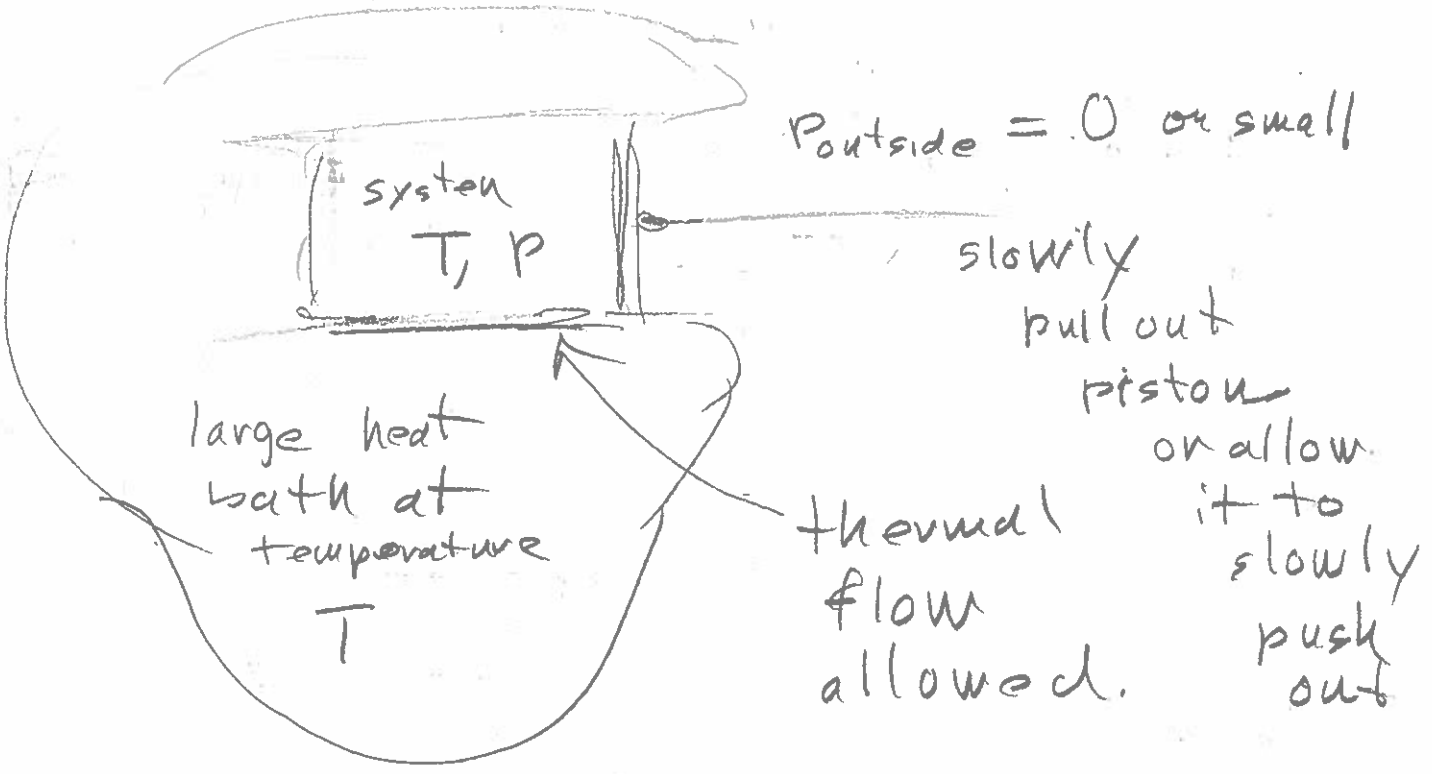
But we have <u>not</u> been adiabatic

$\therefore 0 = \Delta E = \Delta Q + W_w$

$\therefore \Delta Q = W$

du order to keep the system at constant T, Heat energy was added.

Not so hard to do this



The system stays at heat bath temperature as work gets done.

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20.5 Molar Heat Capacities of an Ideal gas

For an ideal gas with a fixed number of degrees of freedom d and assuming energy equipartition

$$E_{int} = \frac{d}{2} n_{mol} R T$$

E_{int}: internal energy (Not internal energy density)

n_{mol}: number of Moles

RT: No Volume dependence at all

We define

$$C_V = \left(\frac{\partial E / n_{mol}}{\partial t}\right) = \left(\frac{d}{2}\right) R$$

d is NOT differential sign here

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Now 1st law in our first form

$$dE = \delta Q - \delta W$$

$\delta W = P\,dV$

Even if we don't know P as function of anything

But for ideal gas

$dE = C_{v\,mol}\,dT$ in all cases.

Volume does NOT have to be constant

but if volume is constant

$dV = 0$

then $\delta Q = dE = C_{v\,mol}\,dT$

and we do call C_v the molar heat capacity for constant volume

C_v is NOT only the molar heat capacity at constant volume

But it is move since $dE = C_{v\,mol}\,dT$ always!

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But say you add δQ and also change volume at constant pressure

An imposed constraint

$C_v n_{mol} dT = dE = \delta Q_p - P dV$ (P for constant pressure)

$= \delta Q_p - d(PV)$

$= \delta Q_p - d(n_{mol} R T)$

$= \delta Q_p - n_{mol} R dT$

$\delta Q_p = (C_v + R) n_{mol} dT$

$\delta Q_p = C_p n_{mol} dT$, define $C_p = C_v + R$

δQ_p: add this much heat a constant pressure

and $dT = \dfrac{\delta Q}{C_p n_{mol}}$

is the temperature increase at constant pressure

$$\therefore \quad C_p = C_V + R$$

$$= \frac{d}{2} R + R$$

$$= \left(\frac{d}{2} + 1\right) R$$

is the heat capacity per mole at constant pressure

(molar heat capacity at constant pressure)

and ONLY that.

20.6 Adiabatic Processes and Adiabatic Index for an Ideal Gas

Ideal gas law

$$pV = n_{mol} R T$$

$$d(pV) = n_{mol} R \, dT$$

$$p\,dV + V\,dp = n_m R\,dT$$

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But now we impose adiabatic constraint

$$\underbrace{\delta Q}_{=0} - P dV = dE = C_V n_{mol} dT$$

Recall always true NOT just at constant volume

$$\therefore \quad n_{mol} dT = \frac{-P dV}{C_V}$$

$$P dV + V dP = -\frac{R}{C_V} P dV$$

$$V dP = -\left(1 + \frac{R}{C_V}\right) P dV$$

$$= -\left(\frac{C_P}{C_V}\right) P dV$$

$$\frac{dP}{P} = -\gamma \frac{dV}{V}$$

where $\gamma \equiv \frac{C_P}{C_V} = \frac{\left(\frac{d}{2}+1\right)R}{\frac{d}{2}R} = \left(\frac{d+2}{d}\right)$ is the adiabatic index

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$$\frac{dP}{P} = -\gamma \frac{dV}{V}$$

Integrating $\ln P = \ln V^{-\gamma} + \text{Constant}$

$$\ln P - \ln V^{-\gamma} = \text{Constant}$$

$$PV^{\gamma} = \text{Constant}$$

and $PV \propto T$

$$V \propto \frac{T}{P}$$

$$\therefore P\left(\frac{T}{P}\right)^{\gamma} = \text{Constant}$$

$$P^{1-\gamma} T^{\gamma} = \text{Constant}$$

$P = \frac{C}{V^{\gamma}}$

$\gamma = \frac{d+2}{d} > 1$

Two adiabatic relations.

Note if $T = \text{Constant}$

$$PV = \text{Constant}$$

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

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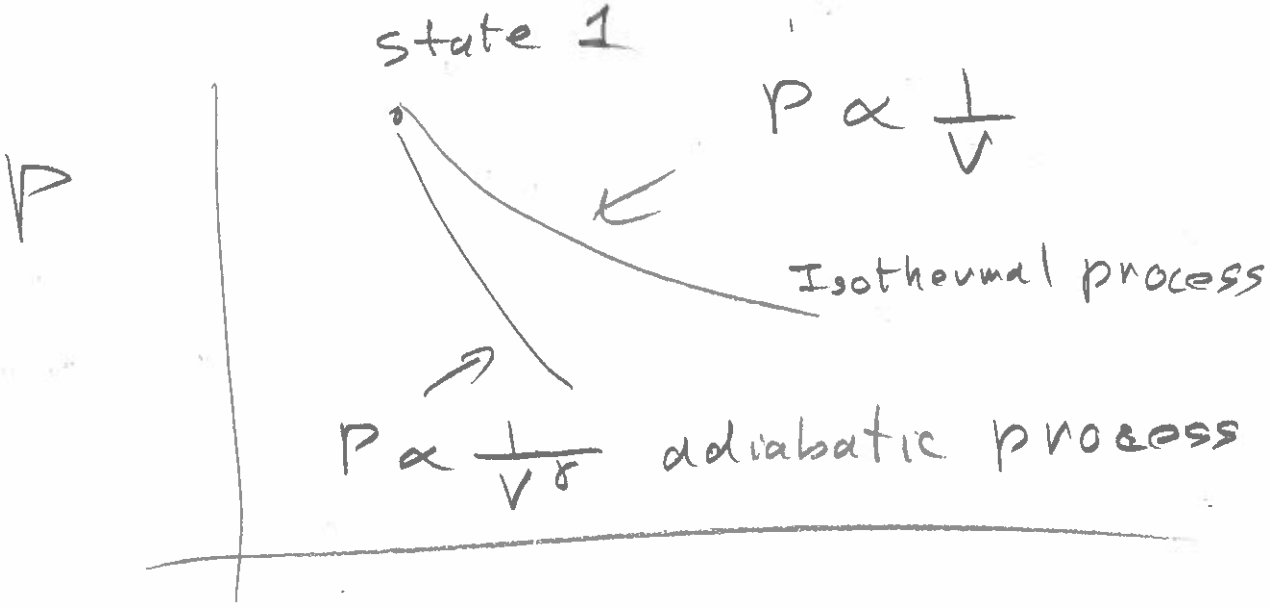
Consider a PV diagram



Heat flow into a isothermal process keeps pressure higher at a give volume than in an adiabatic process where there is no heat flow to keep temperature constant and help sustain pressure