

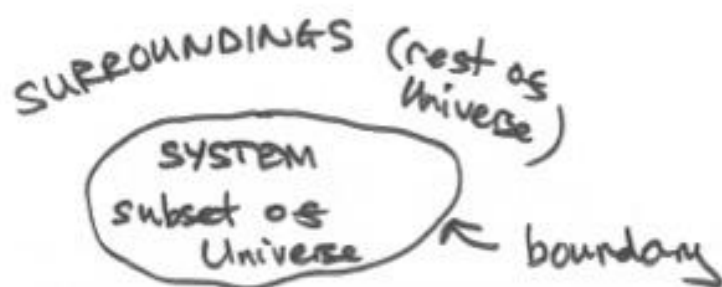
## THERMODYNAMICS

Above the atomic scale we have an "effective theory" of liquids, solids, gases. With properties

$$P, V, T, n$$

What are the laws they obey?

### Set Up



At the boundary:

- closed - no matter in or out
- open - matter can pass
- rigid - no change in system due to external forces
- adiabatic - no heat in or out
- diathermal - heat transfer allowed
- isolated - closed, rigid & adiabatic

FIRST LAW: this can now be framed as energy conservation...

INTERNAL ENERGY: kinetic (& potential) energy stored in the material - for an ideal gas just KE

U is a "function of state" - if you know T & n → U

HEAT: energy transferred between system & environment due to temperature difference

Q: naively  $Q = \Delta U$ .

? +ve means energy added to system

WORK: a force can do work on the system  
 $W = \int \vec{F} \cdot d\vec{x}$  (+ve)

The system can generate forces on boundary eg pressure that do work on the surroundings (-ve)

Thus

$$\Delta U = Q + W$$

For small changes

$$dU = dQ + dW$$

all just increase dU  
{ line means not function of state - we can add heat & work in many ways

## Perpetual Motion Machines Of The First Kind

There is a dishonorable history of people trying to make machines that do work with no energy input (an example will be an PSS). They violate the first law & are impossible. The Patent Office tries to reject these!

## EXPANSION AND COMPRESSION OF GASES



## REVERSIBILITY


Reversible change: process changes system + surroundings. Reversible is both can be returned to initial state.


Atom by atom this is impossible... but if system & surrounds are in thermal  $\equiv$  through out the process... and there's minimal friction... can approximately be there.

## EG irreversible processes

- drop a hot stone in water - can't get heat back into stone.
- make a shock wave that dissipates - never see reverse of this process

Reversible Change 2: best is tiny changes that can be reversed by tiny reverse changes in surroundings  
 ? infinitesimal

eg  sealed cool: vapour  $\rightarrow$  water  
 heat: reverses

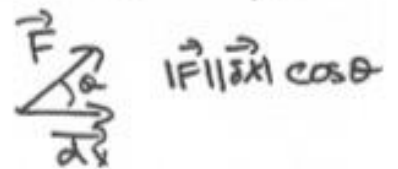
eg  don't ram it in and set up pressure waves!  
 Lots of tiny motions & allow to thermalize at all times!

WORK IN REVERSABLE PROCESSES

work = force  $\times$  distance (in direction of force)

$$= \int \vec{F} \cdot d\vec{x}$$

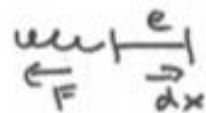
$\leftarrow$  sum little pieces if  $\vec{F}$  or  $d\vec{x}$  change



$$|\vec{F}| |\vec{dx}| \cos \theta$$

eg extending a spring

$$F = -kx$$

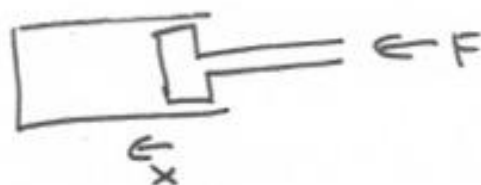


$$\leftarrow F \quad \vec{dx}$$

$$W = \int_{x_1}^{x_2} \vec{F} \cdot d\vec{x} = \int_{x_1}^{x_2} kx dx = \frac{k}{2}(x_2^2 - x_1^2)$$

## Compressing a gas

The force opposes the pressure of the gas



$$F = PA$$

(work done on gas)

$$dW_R = PA \delta x = -P \delta V$$

↑ reversible

↑ volume decreases so  $-(-\delta V)$

$$W_R = - \int P dV$$

## HEAT CAPACITIES

We can be more careful here now:

$$dQ = dU - dW$$

$$C = \frac{dQ}{dT} = \frac{dU}{dT} - \frac{dW}{dT}$$

So  $C$  depends on how much work the system does.

### Constant Volume, $C_V$

Here there is no work done by the gas ( $\delta x = 0$ )

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V$$

which we computed earlier....

### Constant Pressure, $C_P$

If a gas warms & expands it does work on the environment ( $W < 0$ )  $\Rightarrow C_P > C_V$

1st Law  $\delta Q_R = dU - \delta W_R$   
 $= dU + PdV$

For one mole of an ideal gas  $PV = RT_I$   
 $\&$   $dU = C_V dT_I$

At constant pressure  $d(PV) = PdV = R dT_I$

$$\Rightarrow C_P = \frac{\delta Q}{dT_I} = \frac{C_V dT_I + R dT_I}{dT_I}$$

$$C_P = C_V + R$$

eg monatomic gas

$$C_V = \frac{3}{2}R$$

$$C_P = \frac{5}{2}R$$

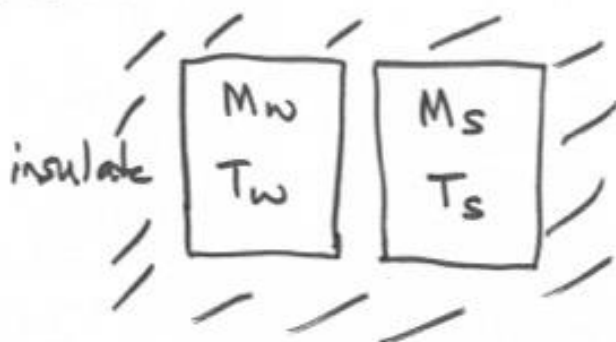
People define

$$\gamma = C_P / C_V$$

$$\gamma_{\text{mono}} = 5/3.$$

### CALORIMETRY

$C_V$  for different substances can be related to that for water by simple heat exchange with no work done



$$M_w C_w (T_S - T_w) = C_s M_s (T_s - T_S)$$

$$C_s = \frac{M_w C_w (T_S - T_w)}{M_s (T_s - T_S)}$$

## EXPANSION AND COMPRESSION OF GASES

- ISOTHERMAL  $T$  constant  $\Rightarrow$   $U$  constant  
ideal gas

$$\Rightarrow Q + W = 0$$

Thus if the gas expands it must take in heat.  
(contracts) (give out)

### Isothermal Compression

Stress: reversible - do things  
slow in thermal contact  
with surroundings

$$W_R = - \int_{V_1}^{V_2} P dV$$

$$\stackrel{\text{ideal gas}}{=} - \int_{V_1}^{V_2} \frac{n_m R T_I}{V} dV$$

$$= - n_m R T_I \int_{V_1}^{V_2} \frac{dV}{V}$$

$$= n_m R T_I \ln(V_1/V_2)$$

Note: if  $V_1 > V_2$  then compression leads to  
the work on the gas.

ADIBATIC  $Q=0$  no heat in or out.

$$\Delta U = W$$

Any work done just changes the internal energy.

### Adiabatic Compression

stress: reversible - do things slowly

$$dU = dW + dQ$$

$\uparrow$  zero for adiabatic

$$dU = -P dV$$

one mole:

$$C_V dT_I = -P dV$$

$\uparrow$   $RT_I/V$

$$\cancel{C_V} \frac{dT_I}{T_I} = -\frac{R}{C_V} \frac{dV}{V}$$

integrate

$$\cancel{C_V} \ln T_I + \frac{R}{C_V} \ln V = \text{const}$$
$$\ln T_I^{\cancel{C_V}} V^{R/C_V} = \text{const}$$



$$\Rightarrow T_I V^{R/C_V} = \text{const}'$$

$$P V \quad V^{R/C_V} = \text{const}''$$

$$P V^{(C_V+R)/C_V} = \text{constant}$$

$$P V^{C_P/C_V} = \text{constant}$$

$$\Rightarrow \boxed{P V^\gamma = \text{constant}}$$

$$\gamma = \frac{C_P}{C_V}$$

$$\gamma_{\text{mono}} = 5/3 ; \quad \gamma_{\text{diatomic}} = 7/5$$

Since  $\gamma > 1$   $P \sim 1/V^\gamma$  falls off more steeply than the isothermal  $P \sim 1/V$ .

This is because as expand also removing energy to do work.

### Work in Adiabatic Compression

$$W_R = - \int_{V_1}^{V_2} P dV$$

$$= - P_1 V_1^\gamma \int_{V_1}^{V_2} \frac{dV}{V^\gamma}$$

$$= - P_1 V_1^\gamma \left[ \frac{V^{1-\gamma}}{1-\gamma} \right]_{V_1}^{V_2}$$

$$= \frac{P_1 V_1}{\gamma-1} \left[ \left( \frac{V_1}{V_2} \right)^{\gamma-1} - 1 \right]$$

$$P_1 V_1^\gamma = P_2 V_2^\gamma \\ = P V^\gamma \text{ in process}$$

If  $V_1 > V_2$   
& compressed  
then  $W_R$  true.

## PV Indicator Diagrams

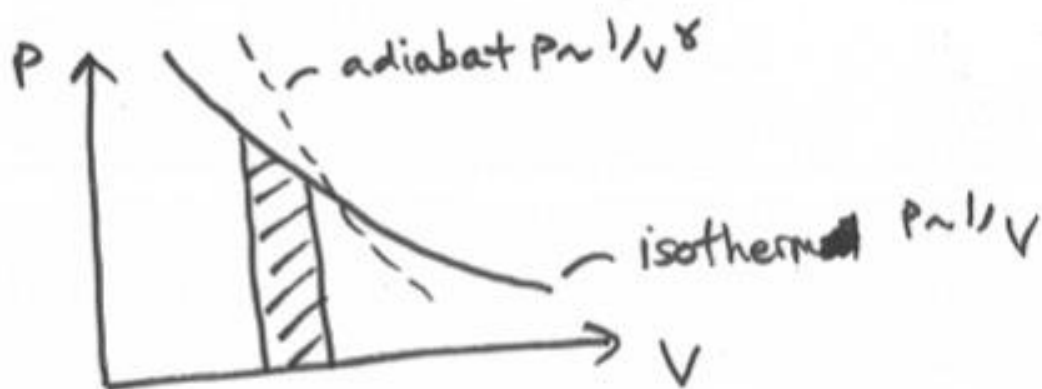
A gas is described by  $N, P, V, T$

But  $N$  is usually fixed...

$$\& PV = NkT$$

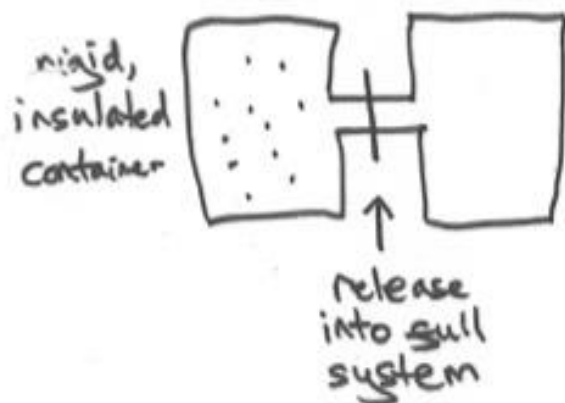
So we have two real variables eg  $\begin{matrix} PV \\ PT \\ VT \end{matrix}$

Most often best to use  $P, V$



Since  $dW = -PdV$  the area under these curves is the work done.

• Joule Expansion



No work is done on surroundings  $W=0$

Adiabatic so  $Q=0$

$\Rightarrow$  the internal energy  $U$  is unchanged

Joule devised this to test if  $U$  depends on  $V$

Is  $U(T, V)$

$$dU = \left( \frac{\partial U}{\partial T} \right)_V dT + \left( \frac{\partial U}{\partial V} \right)_T dV$$

since  $dU=0$

$$dT = - \frac{\left( \frac{\partial U}{\partial V} \right)_T dV}{\left( \frac{\partial U}{\partial T} \right)_V}$$

he measured this to be zero

these are known not to be zero

$$\Rightarrow \left( \frac{\partial U}{\partial V} \right)_T = 0$$

so  $U(T)$  only.