Modern
Day 18

Outline

I Last time

II Heat capacity of Gases

III Inexact differentials and path dependence

IV Return to heat capacity of gases

V What is adiabatic?

- $\Delta Q = \Delta U + \Delta W$

- $\Delta Q = C\Delta T$

  $= cm\Delta T$

  ↑ Solids & liquids

  (i) mass measures how much stuff

  (ii) how heated irrelevant because there is little expansion

Hence heat exchange completely determined by c = specific heat.

I
- Expanding gas
  - $\boxed{dW = PdV}$

- At temp. T each d.o.f gets $\boxed{\tfrac{1}{2}kT \text{ of energy}}$

- $U = N\frac{d}{2}kT$

  $= \frac{d}{2}nRT$

II Measure amount in terms of moles

$$C = \begin{cases} nC_V & \text{(constant volume)} \\ nC_p & \text{(constant pressure)} \end{cases}$$

with C_V (C_p) "molar heat capacity at constant volume (pressure)"

III [Aside on notational lies:

$\Delta U = U_f - U_i$

but $\Delta Q \neq Q_f - Q_i$

What is going on? Let's have a footrace — two volunteers. Alice you run from podium to wall, Bob you run from podium to wall back to podium and back to wall. Go!

Unfair race. Why?

Who travelled a greater net distance? Neither

Who travelled a greater total distance? Bob.

$$d_{net} = \int_{x_i}^{x_f} dx \underset{\uparrow}{=} (x_f - x_i)$$

Fundamental theorem of calculus

$$d_{tot} \neq \int_{x_i}^{x_f} dx \quad \text{instead}$$

$$d_{tot} = \int_{path} |dx|$$

This integral depends on the path that you take, e.g. on how we told Bob to run,

So, in some instances the path you take matters. If we want to know the distance from podium to wall it doesn't, but if we want to travel less total distance it does.

How does this show up in the mathematics?

and there is no way to calculate its value unless you know the details of the path.

In particular, you <u>cannot</u> use the fundamental thm. of calculus for such paths.

When we want to emphasize that a quantity is small but also that calculating sums of that quantity depends on the path you take we use the $đ$ symbol, e.g.

$$đQ \quad \text{and} \quad đW$$

and say that these are <u>inexact</u> differentials. Conversely, if you want to check if something is exact you ask whether you can compute it directly from knowing the current configuration

IV So we now know we should write

$$đQ = dU + đW = dU + PdV$$

Constant volume: $đQ_V = dU = nC_V dT$

Constant pressure: $đQ_p = \underbrace{dU}_{nC_V dT} + \underbrace{PdV}_{nR\,dT}$

always true since it only depends on state. $\rightarrow$

$$= nC_V dT + nR\,dT$$

On the other hand we also have

of the system. For example, in an ideal gas

$$U = \frac{3}{2} NkT$$

and we can calculate U directly from the current temperature without any knowledge of the history of how it got there.

Hence we write dU and say this is an <u>exact</u> differential

$$đQ_p \equiv nC_p dT$$

Setting these two equal gives,

$$\boxed{C_p = C_V + R}$$

But, by equipartition we also have $U = \frac{d}{2} nRT \Rightarrow dU = nC_V dT = \frac{d}{2} nR\,dT$

$$\Rightarrow \boxed{C_V = \frac{d}{2} R} \quad \text{and} \quad \boxed{C_p = \left(\frac{d}{2}+1\right) R}$$

Examples:

Monatomic: $d=3$, so $C_V = \frac{3}{2}R$ $C_p = \frac{5}{2}R$

Diatomic: (rotational but no vibrational) $d=5$, $C_V = \frac{5}{2}R$, $C_p = \frac{7}{2}R$

Polyatomic: (no vibration) $d=6$, $C_V = 3R$, $C_p = 4R$

V We use a cooler to keep our drinks cold.

Adiabatic means: no heat in or out.

Question: How are P and V related during an adiabatic expansion?