Thermal Physics

Meeting XI

I Last time

II How can we cool/heat gases?

III Throttling process

IV Heat Engines

I

- We found

$$C_p - C_v = VT \frac{\alpha^2}{\kappa}$$

α = "Vol. coeff. of expansion"

κ = "Isothermal compressability"

$$\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p ; \quad \kappa \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$$

- We also found

$$dS = \frac{C_v}{T}\, dT + \left(\frac{\partial p}{\partial T}\right)_V dV$$

and proved can get S and E just from

1) $C_v(T, V = V_1)$
2) Eqn of State

- Introduced van der Waals gas

Eqn. of State

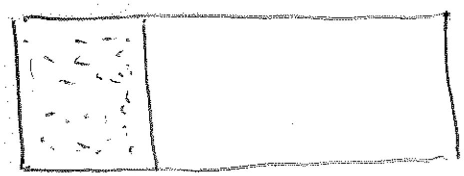
$$\left(p + \frac{a}{v^2}\right)(v - b) = RT$$

with $v = \frac{V}{\nu}$ the molar volume

II Cool/heat gases

How does the temperature

change under free expansion?



Adiabatic $\Rightarrow$ $Q = 0$

Gas does no work in expanding

$$W = 0$$

Nothing interesting for ~~van der W~~ ideal gas

What about van der Waals gas?

$$\mathcal{E}(T_2, v_2) = \mathcal{E}(T_1, v_1)$$

and we found $\mathcal{E}(T, v) = \int_{T_i}^{T_f} c_v dT' - \frac{a}{v} + \text{const},$

so

$$\int_{T_0}^{T_2} c_v(T')\,dT' - \frac{a}{v_2} = \int_{T_0}^{T_1} c_v(T')\,dT' - \frac{a}{v_1}$$

or

$$\int_{T_1}^{T_2} c_v(T')\,dT' = a\left(\frac{1}{v_2} - \frac{1}{v_1}\right)$$

But then

$$\Delta E = 0$$

and so

$$E(T_f, V_f) = E(T_i, V_i).$$

We have shown that

$$E(T, V) = E(T)$$

for ideal gas and so

$$E(T_f) = E(T_i) \Rightarrow \boxed{T_f = T_i}$$

If c_v is roughly T indep in range $T_1 < T' < T_2$ then

$$c_v(T_2 - T_1) = a\left(\frac{1}{v_2} - \frac{1}{v_1}\right)$$

or

$$(T_2 - T_1) = \frac{a}{c_v}\left(\frac{1}{v_2} - \frac{1}{v_1}\right)$$

If $v_2 > v_1 \Rightarrow \frac{1}{v_1} > \frac{1}{v_2}$ and

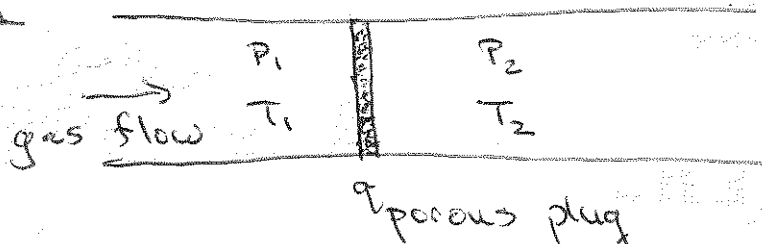
$$T_2 < T_1$$

The temperature is reduced under free expansion

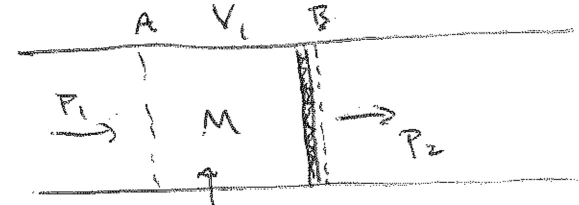
In practice the container messes this up by absorbing heat.

More practical is throttling

III

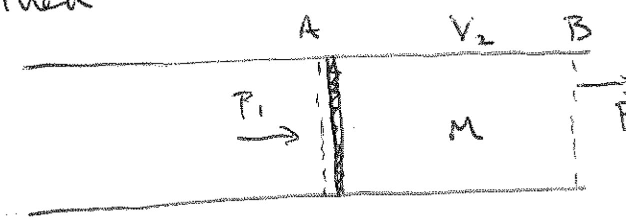


The plug causes a constant pressure difference. What then is the temp. T_2, given T_1 on left?



total mass M of gas

then



$$\Delta E = E_2 - E_1 = E(T_2, p_2) - E(T_1, p_1)$$

But, the gas also does work

$$W = p_2 V_2 - p_1 V_1.$$

It ~~does no heat~~ exchanges no heat

$$Q = 0$$

and so

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

or

$$E_2 + p_2 V_2 = E_1 + p_1 V_1$$

Look familiar? It's the enthalpy

$$H_2 = H_1$$

or

$$H(T_2, p_2) = H(T_1, p_1)$$

Ideal gas:

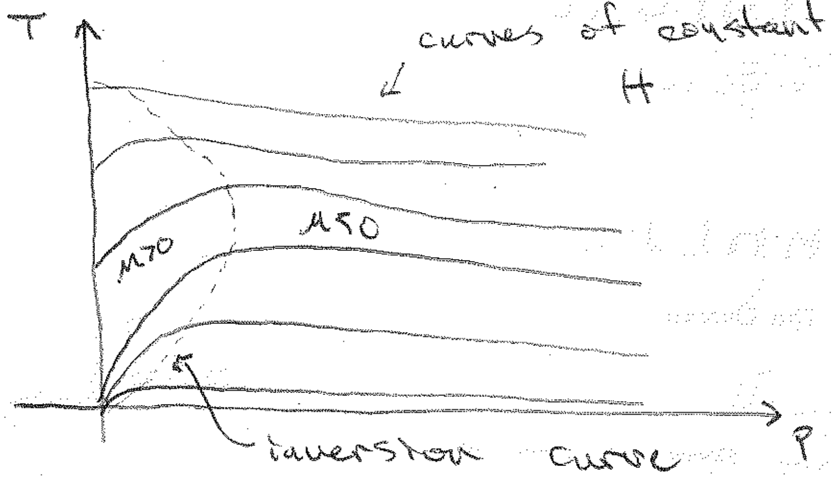
$$H = E + pV = \underset{\text{function of}}{E(T)} + \nu R T$$

so $H = H(T)$ and

$$H(T_2) = H(T_1) \Rightarrow \boxed{T_2 = T_1}$$

Throttling doesn't change the temperature of an ideal gas.

More generally



If $\mu > 0$ then small pressure decrease $\Rightarrow$ small temp. decrease $\rightsquigarrow$ cooling.

Let's find relations for μ:

$$dE = T\,dS - p\,dV$$

$$\Rightarrow \quad dH = T\,dS + V\,dp$$

Here we have $dH = 0$ and want $S(T,p)$ so we get

Read off T_2 from $H(T_1, p_1)$ and p_2.

The curves on this diagram often have maxima

$\Rightarrow$ sometimes throttling cools

and " it heats

Let

$$\mu \equiv \left(\frac{\partial T}{\partial p}\right)_H$$

the "Joule-Thomson" coeff.

$$0 = T\left[\left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp\right] + V\,dp$$

$$\Rightarrow \quad C_p\,dT + \left[T\left(\frac{\partial S}{\partial p}\right)_T + V\right]dp = 0$$

or

$$\left(\frac{\partial T}{\partial p}\right)_H = -\frac{T\left(\frac{\partial S}{\partial p}\right)_T + V}{C_p}$$

Maxwell relation gives

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p = -V\alpha$$

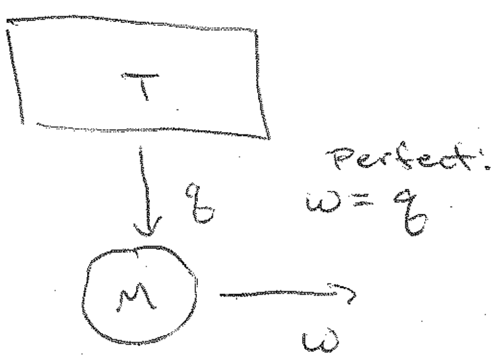
Then

$$\boxed{\mu = \frac{V\alpha T - V}{C_p} = \frac{V}{C_p}(\alpha T - 1)}$$

Throttling is often used to liquefy gases

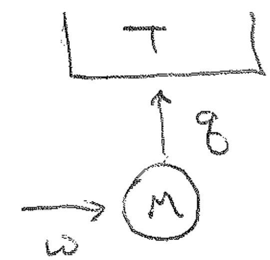
Gas	He	H	N
Max inv. temp (i.e. bndry of $\mu>0$)	34° K	202° K	625° K

Perfectly?



Want: • M to be able to cycle
⇝ ends in same macrostate as it began in

IV Easy to do the following



Reservoir B ends up with increased internal energy

Convention: w = positive work
q = positive heat

Can we invert this?

• M should convert randomly distributed energy of many d.o.f.s to energy of single d.o.f. controlling external param.

<u>Perfect engine impossible</u>:

$$\Delta S \geq 0$$

(ΔS of heat eng., device it does work on and reservoir.)

$$\Delta S_{eng} = 0 \quad \Delta S_{device} = 0$$

$$\Delta S_{res} = \frac{-q}{T_{res}} \geq 0$$

then if $q = w$ we have

$$\frac{q}{T_{res}} = \frac{w}{T_{res}} \leq 0$$

which would imply $w < 0 \Rightarrow$ useless.