Thermal Physics

Meeting IX

I Last time

II Macroscopic Thermodynamics and the ideal gas

III General partial derivative relations

• Entropy can be expressed

$$S(T_b) - S(T_a) = \int_{T_a}^{T_b} \frac{C_y(T')\,dT'}{T'}$$

II Fundamental relation

$$đQ = dE + đW$$

Consider state to be determined by V and E (many other choices possible).

I. • Macro determination of $\bar{E}, W, Q, T$

e.g. $\Delta \bar{E} = -W_{ab}$ thermally insulated

• Heat capacity

$$C_y = \left(\frac{đQ}{dT}\right)_y$$

specific heat

$$c_y = \frac{1}{\nu}\left(\frac{đQ}{dT}\right)_y$$

For quasi-static processes

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

Good starting point for most problems.

Extended example: ideal gas.

$$pV = \nu R T$$

ν: # moles; R: ideal gas constant

We found previously that

$E = E(T)$ no V dependence.

This came from

$$\beta = \frac{\partial \ln \Omega}{\partial E} = \frac{\partial}{\partial E}\left(N \ln V + \ln \chi(E) + \text{const.}\right)$$
$$= \frac{\partial \ln \chi(E)}{\partial E}.$$

Let's prove it again only using the equation of state

$$pV = \nu R T.$$

We also have directly $S = S(T, V)$

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

It follows that

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{1}{T}\left(\frac{\partial E}{\partial T}\right)_V$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T}\left(\frac{\partial E}{\partial V}\right)_T + \frac{\nu R}{V}$$

Suppose $E = E(T, V)$

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

Now,

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

$$\Rightarrow \quad dS = \frac{1}{T} dE + \frac{p}{T} dV$$
$$= \frac{1}{T} dE + \frac{\nu R}{V} dV$$
$$= \frac{1}{T}\left(\frac{\partial E}{\partial T}\right)_V dT + \left[\boxed{\frac{1}{T}}\left(\frac{\partial E}{\partial V}\right)_T + \frac{\nu R}{V}\right] dV$$

Always true that

$$\frac{\partial^2 S}{\partial V \partial T} = \frac{\partial^2 S}{\partial T \partial V}$$

L.H.S is

$$\frac{1}{T}\frac{\partial^2 E}{\partial V \partial T}$$

R.H.S. is

$$= \left[-\frac{1}{T^2}\left(\frac{\partial E}{\partial V}\right)_T + \frac{1}{T}\frac{\partial^2 E}{\partial T \partial V} + 0\right]$$

$$\Rightarrow \quad -\frac{1}{T^2}\left(\frac{\partial E}{\partial V}\right)_T = 0$$

$$\Rightarrow \quad \boxed{\left(\frac{\partial E}{\partial V}\right)_T = 0}$$

E doesn't depend on V!

Specific heats:

$$đQ = dE + p\,dV$$

For

$$c_v \equiv \frac{1}{\nu}\left(\frac{đQ}{dT}\right)_V \overset{đQ = dE}{=} \frac{1}{\nu}\left(\frac{\partial E}{\partial T}\right)_V$$

Because $E = E(T)$ for an ideal gas we see that c_v does not depend on V! Now,

$$dE = \left(\frac{\partial E}{\partial T}\right)_V dT$$

Then

$$c_p = \frac{1}{\nu}\left(\frac{đQ}{dT}\right)_p$$

gives

$$c_p = c_v + R$$

and as we claimed $c_p > c_v$.

Define

$$\gamma \equiv \frac{c_p}{c_v} = 1 + \frac{R}{c_v}$$

So,

$$dE = \nu c_v\,dT$$

for an ideal gas.

What about c_p?

$$đQ = \nu c_v\,dT + p\,dV$$

Constant p implies

$$p\,dV = \nu R\,dT$$

and

$$đQ = \nu c_v\,dT + \nu R\,dT$$

Comparison w/ micro calculations:

Recall

$$\Omega(E) = \overset{\text{constant}}{B}\, V^N E^{3N/2}$$

$$\Rightarrow \ln\Omega = \ln B + N\ln V + \frac{3N}{2}\ln E$$

and

$$\beta = \frac{\partial \ln\Omega}{\partial E} = \frac{3N}{2}\frac{1}{E}$$

or

$$\boxed{E = \frac{3}{2}NkT}$$

$$= \frac{3}{2}\nu(N_a k)T = \frac{3}{2}\nu RT$$

Then

$$c_v = \frac{1}{\nu}\left(\frac{\partial E}{\partial T}\right)_V = \frac{3}{2}R$$

$$= 12.47 \; \frac{J}{{}^\circ K \text{ mole}}$$

and

$$c_p = \frac{3}{2}R + R = \frac{5}{2}R$$

$$\gamma = \frac{c_p}{c_v} = \frac{5/2\,R}{3/2\,R} = \frac{5}{3}$$

Let's elliminate dT

$$0 = c_v\left(\frac{V}{R}dp + \frac{p}{R}dV\right) + p\,dV$$

$$= \left(\frac{c_v}{R} + 1\right)p\,dV + \frac{c_v V}{R}dp$$

or

$$(c_v + R)\,p\,dV + c_v V\,dp = 0$$

Dividing through by $c_v p V$ gives

$$\gamma\frac{dV}{V} + \frac{dp}{p} = 0$$

<u>Adiabatic expansion</u>:

<u>If</u> T is held fixed and a gas expands

$$pV = \text{const.}$$ (isothermal expansion)

What about adiabatic expansion?

$$đQ = 0 = \nu c_v dT + p\,dV$$

The equation of states gives

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

As long as γ is T indep we can integrate to get

$$\gamma \ln V + \ln p = \text{const}$$

or

$$\ln pV^\gamma = \text{const}$$

$$\Rightarrow \boxed{pV^\gamma = \text{const.}}$$

Lots of forms

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

I'll let you read over the entropy calculation – same idea as yesterday's calculations.

III Always begin with

$$đQ = T\,dS = dE + p\,dV$$

i) <u>Take S and V as indep. vars</u>

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

$$\frac{\partial^2 E}{\partial V \partial S} = \frac{\partial^2 E}{\partial S \partial V}$$

(as you proved!). So,

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$$

Can keep playing this game.

ii) <u>Choose S and p as indep. vars</u>

So $E = E(S,V)$ and

$$dE = \left(\frac{\partial E}{\partial S}\right)_V dS + \left(\frac{\partial E}{\partial V}\right)_S dV$$

This means that

$$T = \left(\frac{\partial E}{\partial S}\right)_V$$

$$-p = \left(\frac{\partial E}{\partial V}\right)_S$$

Cool! The variables T, S, p, V must be related to give an exact dE. How? By

What is a good state variable that depends on S and p?

Let's find out.

$$d(pV) = V\,dp + p\,dV$$

$$\Rightarrow \quad p\,dV = -V\,dp + d(pV)$$

So,

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

$$= T\,dS + V\,dp - d(pV)$$

$$\Rightarrow d(E + pV) = T\,dS + V\,dp$$

If we let $H = E + pV$, give it the name enthalpy, then

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

By construction $H(S, p)$ so

$$dH = \left(\frac{\partial H}{\partial S}\right)_p dS + \left(\frac{\partial H}{\partial p}\right)_S dp$$

and we see

$$T = \left(\frac{\partial H}{\partial S}\right)_p \quad \text{and} \quad V = \left(\frac{\partial H}{\partial p}\right)_S$$

We must have

$$\frac{\partial^2 H}{\partial p\,\partial S} = \frac{\partial^2 H}{\partial S\,\partial p}$$

so

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

Intro $F = E - TS$, call it "Helmholtz free energy"

By construction $F = F(T, V)$

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

So,

$$S = -\left(\frac{\partial F}{\partial T}\right)_V \qquad p = -\left(\frac{\partial F}{\partial V}\right)_T$$

and

$$\frac{\partial^2 F}{\partial V\,\partial T} = \frac{\partial^2 F}{\partial T\,\partial V}$$

(iii) Take T and V as indep. var.s

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

$$\Rightarrow \quad dE - d(TS) = -S\,dT - p\,dV$$

$$\Rightarrow \quad d(E - TS) = -S\,dT - p\,dV$$

gives,

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V .$$

Finally (iv) Take T and p as indep. var.s

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

$$\Rightarrow \quad dE - d(TS) + d(pV) = -S\,dT + V\,dp$$

$$\Rightarrow \quad dG = -S\,dT + V\,dp$$

where

$$G = E - TS + pV = F + pV$$

and is naturally a function of

$$G = G(T, p)$$

Then

$$dG = \left(\frac{\partial G}{\partial T}\right)_p dT + \left(\frac{\partial G}{\partial p}\right)_T dp$$

and

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

with

$$\frac{\partial^2 G}{\partial p\,\partial T} = \frac{\partial^2 G}{\partial T\,\partial p}$$

comes

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