

Thermal Physics

Meeting X

I Using

$$dE = T ds - p dV$$

we found

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

I Last time

II Specific heats

III Entropy and Internal Energy

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

Thermodynamic potentials:

$$E = E(S, V)$$
$$dE = T ds - p dV$$
$$H = H(S, p) = E + pV$$
$$dH = T ds + V dp$$

$$F = E - TS = F(T, V)$$

$$dF = -S dT - p dV$$

$$G = G(T, p) = E - TS + pV$$

$$dG = -S dT + V dp$$

II Is there a general relation between C_V and C_P ?

Well,

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

$$C_P = \left(\frac{\partial Q}{\partial T} \right)_P = T \left(\frac{\partial S}{\partial T} \right)_P$$

Experimentally easiest to control

T and P, so take $S = S(T, P)$,

$$\begin{aligned} \partial Q = T dS &= T \left[\left(\frac{\partial S}{\partial T} \right)_P dT + \left(\frac{\partial S}{\partial P} \right)_T dP \right] \\ &= C_P dT + T \left(\frac{\partial S}{\partial P} \right)_T dP \end{aligned}$$

$$\text{or } C_V = C_P + T \left(\frac{\partial S}{\partial P} \right)_T \left(\frac{\partial P}{\partial T} \right)_V \quad (1)$$

not easily measured

$$\text{But, } \left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_P$$

and we can define "volume coeff. of expansion"

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad \text{intensive}$$

Also, $\left(\frac{\partial P}{\partial T} \right)_V$ not convenient, go to

Now, think of
to find

$$\partial Q = C_P dT + T \left(\frac{\partial S}{\partial P} \right)_T dP$$

$$\left[\left(\frac{\partial Q}{\partial T} \right)_V dT + \left(\frac{\partial Q}{\partial P} \right)_T dP \right]$$

Heat transfer at constant volume

is then given by $dV=0$,

$$\left(\frac{\partial Q}{\partial T} \right)_V = C_P + T \left(\frac{\partial S}{\partial P} \right)_T \left(\frac{\partial P}{\partial T} \right)_V$$

$$V = V(T, P) \quad \text{so}$$

$$dP \left(\frac{\partial V}{\partial P} \right)_T + T \left(\frac{\partial S}{\partial P} \right)_T dP = dV$$

When $dV=0$ we get

$$0 = -V \left(\frac{\partial P}{\partial P} \right)_T \frac{dP}{\left(\frac{\partial V}{\partial P} \right)_T}$$

"Isothermal compressibility"

$$\kappa \equiv - \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

$$P = P(T, V) \quad P \approx 1/b$$

Then

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{\alpha}{\kappa}$$

Putting all this into (1) gives

$$C_V = C_P - T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial p}{\partial T}\right)_V \\ = C_P + T(-V\alpha) \frac{\alpha}{\kappa}$$

or

$$C_P - C_V = VT \frac{\alpha^2}{\kappa}$$

Then,

$$C_P - C_V = VT \cdot \frac{1}{T^2} \cdot P \\ = \frac{\gamma R T}{T} = \gamma R$$

or

$$C_P - C_V = R \quad \checkmark$$

Limiting properties near absolute zero:

2nd law $T \rightarrow 0 \quad S \rightarrow S_0$

Ideal gas again:

$$pV = \gamma RT$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{\gamma R}{p}$$

$$\text{So } \alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P = \frac{\gamma R}{pV} = \frac{1}{T}$$

$$\text{Also, } \left(\frac{\partial V}{\partial p}\right)_T = \frac{\partial}{\partial p} \left(\frac{\gamma RT}{p}\right) = -\frac{\gamma RT}{p^2} \\ = -\frac{V}{p}$$

$$\Rightarrow \kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial p}\right)_T = \frac{1}{p}$$

This implies

$\frac{\partial S}{\partial T}$ is finite as $T \rightarrow 0$

and hence

$$C_V \rightarrow 0, \quad C_P \rightarrow 0 \\ \text{as } T \rightarrow 0$$

Even easier for

$$S(T) - S(0) = \int_0^T \frac{C_V(T')}{T'} dT' \\ \text{finite} \Rightarrow C_V \rightarrow 0 \text{ as } T \rightarrow 0$$

We also learn from 3rd law that

$$\left(\frac{\partial S}{\partial p}\right)_T \rightarrow 0 \text{ as } T \rightarrow 0$$

$$\Rightarrow \alpha \rightarrow 0 \text{ as } T \rightarrow 0$$

So doesn't depend on the external param.s

But k is finite. Then

$T \propto^2$ goes rapidly to zero as $T \rightarrow 0$.

$$\text{And } \frac{C_p - C_v}{C_v} \rightarrow 0 \text{ as } T \rightarrow 0$$

because $C_p - C_v$ decays even faster than C_v .

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial F}{\partial T}\right)_V \quad (\text{Maxwell Rel.})$$

Then

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

The R.H.S. can be evaluated if we know the eq. of state. Again

$$C_v = C_x(T, V) = T \left(\frac{\partial S}{\partial T}\right)_V$$

then

III Entropy and Internal Energy

Energy

Take T and V indep then

$$S = S(T, V)$$

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

We have

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

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

$$\frac{NkT}{S^2} = T$$

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

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

$$\left(\frac{\partial C_v}{\partial T}\right)_V = T \left(\frac{\partial^2 F}{\partial T^2}\right)_V$$

This goes as follows, 75%

$$C_v(T, V) = C_v(T, V_1) + \int_{V_1}^V \left(\frac{\partial C_v}{\partial V} \right)_T dV'$$

Then we use

$$ds = \frac{C_v}{T} dT + \left(\frac{\partial F}{\partial T} \right)_V dV$$

to get

$$s(T, V) - s(T_0, V_0) =$$

$$dE = C_v dT + \left[T \left(\frac{\partial F}{\partial T} \right)_V - P \right] dV$$

as well as

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

$$\Rightarrow \left(\frac{\partial E}{\partial V} \right)_V = C_v$$

$$\left(\frac{\partial E}{\partial T} \right)_V = T \left(\frac{\partial F}{\partial T} \right)_V - P$$

And again the B.H.S can be solved from the eqn. of state.

This is all building to the question:

If everything is determined once you know S , what experimental

knowledge do you need to determine S ?

Ans.

1.) $C_v(T, V=V_1)$

2.) Eqn. of state.

$$\left[s(T, V) - s(T_0, V) \right] + \left[s(T_0, V) - s(T_0, V_0) \right]$$

and so

$$s(T, V) - s(T_0, V_0) = \int_{T_0}^T \frac{C_v(T', V)}{T'} dT' + \int_{V_0}^V \left(\frac{\partial p(T_0, V')}{\partial T} \right) dV'$$

A similar line of argument gives $E(T, V)$

$$dE = T ds - P dV$$

Consider a gas with the eqn. of state

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

where $v = V/\nu$ is the molar volume.

$\frac{a}{v^2}$ represents long-range

interaction drawing gas together

b short range repulsion

while,

$$\left(\frac{\partial cv}{\partial v}\right)_T = T \left(\frac{\partial^2 p}{\partial T^2}\right) = T \left(\frac{\partial}{\partial T}\right)_v \left(\frac{R}{v-b}\right) = 0$$

as in the ideal gas case. If we assume c_v is roughly T independent then

$$de = c_v dT + \frac{a}{v^2} dv$$

leads to

$$e(T, v) - e(T_0, v_0) = c_v \Delta T - \left(\frac{a}{v}\right) \Big|_{v_0}^{v_1}$$

Solving for p ,

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

Then

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{(v-b)}$$

and

$$\left(\frac{\partial e}{\partial v}\right)_T = T \left(\frac{\partial^2 p}{\partial T^2}\right)_v - p = \frac{RT}{(v-b)} - p = \frac{a}{v^2}$$

or,

$$e(T, v) = c_v T - \frac{a}{v} + \text{const.}$$