CHAPTER 4B

4-5. Consequences of the First Law

The internal energy of a pure substance in a state of equilibrium is a function of the state variables;

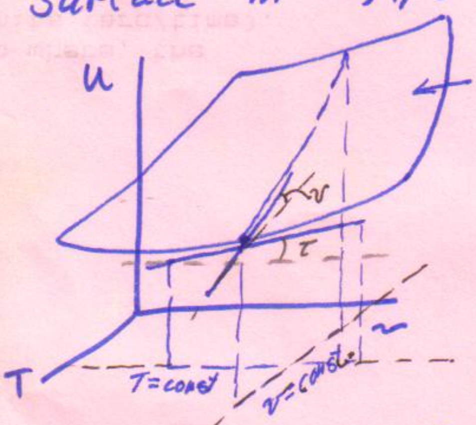
$$u = u(P, v, T)$$

This is called the energy equation.
It can not be derived from the equation of state.
Since P, v, & T are related thru the equation of state, any two vars. define a state, and, hence, u is a function of only 2 independent vars.

T and v Independent: $\quad u = u(T, v)$

Then $$du = \left(\frac{\partial u}{\partial T}\right)_v dT + \left(\frac{\partial u}{\partial v}\right)_T dv \qquad 4\text{-}1$$

The two partials are the slopes of the energy surface in u, T, v space.



In diagram $\tan \tau = \left(\frac{\partial u}{\partial v}\right)_T$

Similarly for other partial.

$$\tan v = \left(\frac{\partial u}{\partial T}\right)_v$$

Assume only configuration work: $\quad d'w = P\,dv$

Now the 1st law is: $$d'q = du + d'w$$
$$= du + P\,dv \qquad (4\text{-}2)$$

subs. 4-1 into 4-2:

$$d'q = \left(\frac{\partial u}{\partial T}\right)_v dT + \left(\frac{\partial u}{\partial v}\right)_T dv + P\,dv$$

Collecting coefs of dT & dv

$$d'q = \left(\frac{\partial u}{\partial T}\right)_v dT + \left[P + \left(\frac{\partial u}{\partial v}\right)_T\right] dv \qquad 4-3$$

This applies to any substance and any reversible process.

Now consider an isochoric process : $dv = 0$

Now, since $C_v = \left(\frac{d'q}{dT}\right)_v$ $d'q = c_v dT$ from experiment.

So 4-3 becomes

$$d'q = \left(\frac{\partial u}{\partial T}\right)_v dT = C_v dT$$

or

$$\boxed{C_v = \left(\frac{\partial u}{\partial T}\right)_v} \qquad 4.4$$

Hence, measurement of C_v yields the rate of change of u with T at const. v.

$\left(\partial u/\partial T\right)_v$ may be substituted for C_v in any equation or vice-versa.

Hence, for any reversible process, the 1st law is

$$\boxed{d'q = C_v dT + \left[P + \left(\frac{\partial u}{\partial v}\right)_T\right] dv} \qquad 4-5$$

Now we seek a relationship between C_p and C_v.
Consider an isobaric process: $dP = 0$
Then

$$d'q_{P} = C_p \, dT_P$$

From 4-5

$$d'q_{P} = c_p \, dT_P = C_v \, dT_P + \left[P + \left(\frac{\partial u}{\partial v}\right)_T\right] dv_P$$

$\div$ by dT_P and rearrange:

$$c_p = C_v + [P + (\partial u/\partial v)_T](dv/dT)_p$$

$$c_p - c_v = \left[P + (\partial u/\partial v)_T\right](dv/dT)_p \qquad \text{4-6}$$

Whether $c_p > c_v$ depends on sign of term on right.

Now consider an isothermal process, that is, dT = 0: Equation (4-5) becomes

$$d'q = \left[P + \left(\frac{\partial u}{\partial v}\right)_T\right] dv_T$$

$$d'q = P\, dv_T + \left(\frac{\partial u}{\partial v}\right)_T dv_T \qquad \text{(4-7)}$$

The last term in the above equation is just du for an isothermal process. See equation (4-1) above. Hence

$$d'q = P\, dv_T + du \qquad \text{(4-7B)}$$

This says that the heat supplied to a system during an isothermal, reversible process equals the sum of the work done by the system plus the change in the increase in its internal energy. Hence, there can be an exchange of heat of a system with its surroundings without a change in temperature. For this case we can say that $C_T = \pm\infty$. Equation (4-8) also says that if the internal energy of a system remains constant, then the work the system does is equal to the heat that flows into the system.

T and P Independent:

Recall that enthalpy is a function of state variables, h = h(P, T, v) and therefore, it has an exact total differential,

$$dh = (\partial h/\partial T)_P dT + (\partial h/\partial P)_T dP. \qquad \text{(4-9)}$$

Now h = u + Pdv.   So dh = du + Pdv + vdP.

Solve for du:

$$du = dh - Pdv - vdP.$$

Insert this into the 1st law: d'q = du + Pdv and we get:

$$d'q = dh - Pdv - v\, vdP + Pdv, \text{ or}$$

$$d'q = dh - vdP \qquad (4\text{-}10)$$

Substitute for dh in the latter using equation (4-9) to obtain

$$đq = \left(\frac{\partial h}{\partial T}\right)_P dT + \left[\left(\frac{\partial h}{\partial P}\right)_T - v\right] dP \qquad (4\text{-}11)$$

Now consider an isobaric process so dP = 0

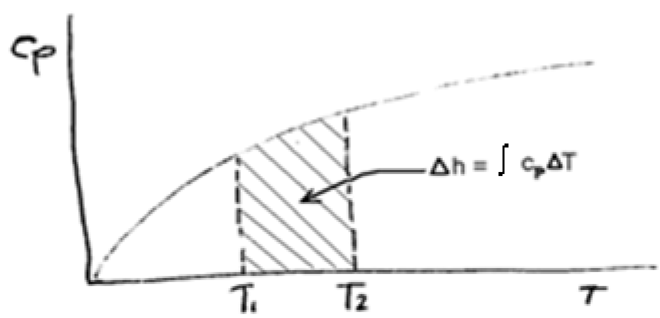
$$đq = \left(\frac{\partial h}{\partial T}\right)_P dT \qquad (4\text{-}11B)$$

Since $c_P = \frac{đq}{dT}$, it follows that $đq = c_P\, dT$. Comparing this expression for $đq$ with (4-12), we conclude that

$$c_P = \left(\frac{\partial h}{\partial T}\right)_P \qquad (4\text{-}12)$$

or $$dh = c_P\, dT$$

then $\Delta h = \int c_P\, dT$, which is shown as the area under the curve in the T-c_P plane.



Then (4-11) becomes

$$d'q = c_p\,dT + \left[\left(\frac{\partial h}{\partial P}\right)_T - v\right] dP \qquad \text{(4-13)}$$

which is quite general.

Now consider isochoric proc., $dv = 0$

$$d'q_v = c_v\,dT_v = c_p\,dT_v + \left[\left(\frac{\partial h}{\partial P}\right)_T - v\right] dP_v$$

$\div\, dT_v$

$$c_v = c_p + \left[\left(\frac{\partial h}{\partial P}\right)_T - v\right] (\partial P/\partial T)_v$$

or

$$c_p - c_v = -\left[\left(\frac{\partial h}{\partial P}\right)_T - v\right] \left(\frac{\partial P}{\partial T}\right)_v \qquad \text{(4-14)}$$

P and v independent, so u= u(P,v):

$$du = \left(\frac{\partial u}{\partial p}\right)_v dp + \left(\frac{\partial u}{\partial v}\right)_p dv \qquad \text{S\&S (4-17)}$$

Now, $du = d'q - p\,dv$ 1st Law

or $d'q = du + p\,dv$

From (4-17) for du:

$$d'q = \left(\frac{\partial u}{\partial p}\right)_v dp + \left(\frac{\partial u}{\partial v}\right)_p dv + P\,dv$$

$$d'q = \left(\frac{\partial u}{\partial p}\right)_v dp + \left[P + \left(\frac{\partial u}{\partial v}\right)_p\right] dv \qquad (4\text{-}17B)$$

At P=const. $d'q_p = c_p\,dT_p$

From (4-17B) $c_p\,dT_p = \left[P + \left(\frac{\partial u}{\partial v}\right)_p\right] dv$

$c_p\left(\frac{\partial T}{\partial v}\right)_p = P + \left(\frac{\partial u}{\partial v}\right)_p$ From the definition of β in Chp. 3.2 we get

$$\boxed{\frac{c_p}{v\beta} - P = \left(\frac{\partial u}{\partial v}\right)_P} \qquad (4\text{-}17C)$$

Isometric: $v = \text{const.}$ $d'q = c_v\,dT$

$$d'q = \left(\frac{\partial u}{\partial p}\right)_v dp = c_v\,dT$$

$$c_v\underbrace{\left(\frac{\partial T}{\partial p}\right)_v}_{=\kappa/\beta} = \boxed{\left(\frac{\partial u}{\partial p}\right)_v = \frac{\kappa c_v}{\beta}} \qquad (4\text{-}17D)$$

This is actually S&S (4-18) with the partials evaluated.

End of Chapter 4B