Let us apply clausius clapeyron Equation to SUBLIMATION PROCESS

Let us represents the specific volume of Solid, liquid and vapour by v_s, v_l and v_v respectively

and different latent heats as

l_s = Latent Heat of sublimation

l_v = Latent Heat of vaporization

and l_f = Latent Heat of fusion (melting)

Using these notation the clapeyron's Equation for sublimation process can be written as

$$\frac{dP}{dT} = \frac{l_s}{T(v_v - v_s)} \qquad (A)$$

Sublimation process takes place at low pressure and at this pressure vapour can be regarded as ideal gas

so $v_v \simeq RT/P$

at very small pressure $v_v \gg v_s$

so eq (A) will result in

$$\frac{dP}{dT} = \frac{l_s}{T\vartheta_v} = \frac{l_s}{T \cdot \frac{RT}{P}}$$

$$l_s = \frac{R\,dP/P}{dT/T^2} = -R\,\frac{d(\ln P)}{d(1/T)}$$

That means the value of l_s can be estimated from slope of $\ln P$ vs $1/T$ curve

l_s = R × slope of $\ln P$ vs $1/T$ curve

* vapour pressure of solids are usually measured over a very short range of temp.
In such a short range curve follows a straight line

* But it has been found that l_s changes with temperature
* If the data in a wider-temperature range is available then the variation in l_s can be observed.

HERE COMES THE KIRCHOFF'S LAW which gives a relation that how l_s changes with temperature.

— An infinitesimal change of molar enthalpy between two states of equilibrium

$$dH = TdS + VdP \qquad (B)$$

Using second Tds equation

$$dH = C_p dT - T\left.\frac{\partial V}{\partial T}\right|_P dP + V dP$$

$$= C_p dT + \left[V - T\left.\frac{\partial V}{\partial T}\right|_P\right] dP \qquad (C)$$

$$= C_p dT + \left[V - TV\alpha\right] dP$$

where α = coefficient of volume expansion at constant P

If the two states ies the process are represented by P_i, T_i and P_f, T_f

then the change in specific enthalpy

$$h_f - h_i = \int_i^f C_p dT + \int_i^f v(1 - T\alpha)\, dP$$

Let i and f state be defined as

i State : zero pressure and zero absolute temperature

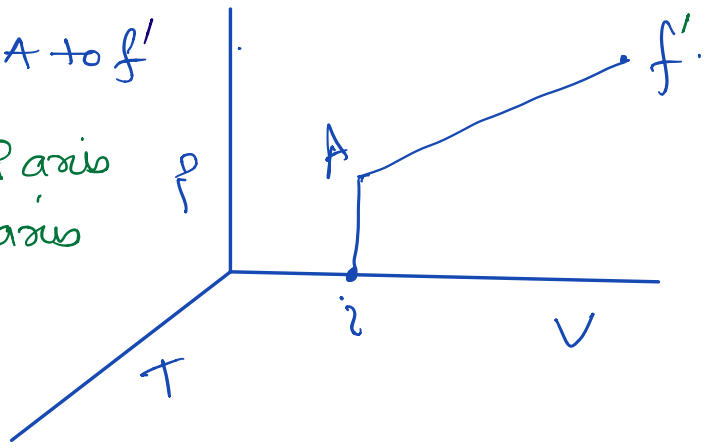
f state = Saturated Solid i.e. Solid about to Sublimate

The i to f process can be considered to be via A as shown in figure

i to A and then A to f'

iA ⇒ Parallel to P axis

Af' ⇒ Parallel to T axis



h_f^s = final enthalpy of solid

h_0^s = initial enthalpy of solid

So $h^s - h_0^s = \int_i^A V(1-T\alpha)\,dP + \int_A^{f'} C_p\,dT$

$= \int_0^P v^s\,dP + \int_0^T C_p^s\,dT$

v^s = molar volume of solid at absolute zero $[V(1-0\alpha) = V = V^s]$

C_p^s = molar heat capacity of solid

Generally the pressure of sublimation curve is very small so

$$h^s = \int_0^T C_p^s \, dT + h_0^s \qquad (c)$$

For solids C_p^s does not change too much with pressure so the value of C_p^s at atmospheric pressure will be taken even low pressure. (It is an approximation)

* Considering that at such a low pressure the saturated vapour may be considered to follow ideal gas equation.

* So considering the general equation

$$C_p = \left(\frac{\partial h}{\partial T}\right)_p$$

$$dh^v = C_p^v \, dT$$

$$\int dh^v = h_g^v - h_0^v$$

or $$h^v = \int_0^T C_p^v \, dT + h_0^v$$

h_0^v = specific enthalpy of saturated vapour at absolute zero

* Now considering the sublimation process of 1 mole of a solid at T and P

$$l_s = h^v - h^s$$

$$= \int_0^T C_p^v \, dT - \int_0^T C_p^s \, dT + h_0^v - h_0^s$$

as both the integrals approaches zero for $T \to 0$

l_{so} or l_0 = heat of Sublimation at absolute zero

$$l_0 = h_0^v - h_0^s$$

$$\text{so } l_s = \int_0^T C_p^v \, dT - \int_0^T C_p^s \, dT - l_0$$

THIS IS KIRCHOFF'S Equation

which is an approximate equation subject to the fact that pressure is low enough to consider the saturated vapour to behave as an ideal gas