Van't Hoff reaction isochore.

Van't Hoff reaction isochore can be obtained by combining van't Hoff isotherm with Gibbs - Helmholtz equation.

We know,

The Van't Hoff isotherm equation as

$$-\Delta G = RT \ln K_p - RT \Sigma n \ln p \quad \text{——} \quad (1)$$

Differentiating with respect to temperature at constant Pressure we have,

$$-\left[\frac{\partial(\Delta G)}{\partial T}\right] = RT \frac{d}{dT} \ln K_p + R \ln K_p - RT \frac{d}{dT} \Sigma n \ln p - R \Sigma n \ln p$$

But $RT \frac{d}{dT} \Sigma n \ln p = 0$, as this arbitary pressure is not the function of Temperature T.

Hence,

$$-\left[\frac{\partial(\Delta G)}{\partial T}\right]_p = RT \frac{d}{dT} \ln K_p + R \ln K_p - R \Sigma n \ln p$$

or, multiplying both side by T,

$$-T\left(\frac{\partial(\Delta G)}{\partial T}\right)_p = RT^2 \frac{d}{dT} \ln K_p + (RT \ln K_p - RT \Sigma n \ln p) \quad (2)$$

From equation (1) we get

$$-T\left[\frac{\partial(\Delta G)}{\partial T}\right]_p = RT^2 \frac{d}{dT} \ln K_p - \Delta G \quad \text{——} \quad (3)$$

or $\Delta G - T\left[\frac{\partial(\Delta G)}{\partial T}\right]_p =$

The Gibbs - Helmholtz equation is given as

$$\Delta G = \Delta H + T\left[\frac{\partial(\Delta G)}{\partial T}\right]_p$$

$$\text{or,} \quad \Delta G - T\left[\frac{\partial(\Delta G)}{\partial T}\right]_p = \Delta H \quad \text{——} \quad (4)$$

And we know from equation (3)

$$\Delta G - T\left[\frac{\partial(\Delta G)}{\partial T}\right]_p = RT^2 \frac{d}{dT} \ln K_p \quad (5)$$

From eqn (4) and (5)

$$\Delta H = RT^2 \frac{d}{dT} \ln K_p$$

The above equation is known as
Van't Hoff reaction Isochore.

When the Vant hoff Isochore is applied to the chemical reaction. It is integrated between Temperature T_1 and T_2 at which the equilibrium Constant are K_{P_1} and K_{P_2} respec

On assuming that ΔH remains Constant.

i.e $$d \ln K_P = \frac{\Delta H}{R} \frac{dT}{T^2}$$

$$\ln K_{P_1} - \ln K_{P_2} = -\frac{\Delta H}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$= -\frac{\Delta H}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

or, $$\ln \frac{K_{P_1}}{K_{P_2}} = -\frac{\Delta H}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

Now, We can Calculate the enthalpy change when equilibrium Constant data at two different temperature is given.