

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

$$-\Delta G = RT \ln K_p - RT \sum n \ln P \quad \text{--- (1)}$$

Differentiating with respect to temperature at constant pressure we have,

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

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

Hence,

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

or, multiplying both side by T ,

$$-T \left(\frac{\partial(\Delta G)}{\partial T}\right)_P = RT^2 \frac{d}{dT} \ln K_p + (RT \ln K_p - RT \sum n \ln P) \quad \text{--- (2)}$$

From equation (1) we get

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

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

The Gibbs-Helmholtz equation is given as

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

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

And we know from equation (3)

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

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 Van't 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} respectively.

① By assuming that ΔH remains constant.

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

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

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

Now, we can calculate the enthalpy change when equilibrium constant data at two different temperature is given. —

