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Topic :– Thermodynamics

Van't Hoff's reaction Isochore :–

The Van't Hoff's reaction Isochore can be derived by differentiating Van't Hoff's reaction isotherm with respect to temperature at Constant Volume

At Constant volume, the change in free energy is not given by $-\Delta G$ but by $-\Delta A$.

Thus We can write

$$-\Delta A = RT\log K_c - RT\sum n\log c$$

Differentiating the above equation with respect to temperature at Constant Volume

$$\left[\frac{\partial(-\Delta A)}{\partial T}\right]_V = RT\frac{d}{dT}(\log K_c) + R\log K_c$$
$$- R.T.\frac{d}{dT}\left(\sum n\log c\right) - R\sum n\log c$$

But $RT\dfrac{d}{dT}\sum n\log c = 0$

As the arbitrary Concentration is not regarded as a function of temperature.

Hence $\left[\frac{\partial(-\Delta A)}{\partial T}\right]_V = RT\frac{d}{dT}(\log K_c) + R\log K_c - R\sum n \log c$

$$-T\left(\frac{\partial(-\Delta A)}{\partial T}\right)_V = RT^2\frac{d}{dT}(\log K_c) + RT\log K_c - RT\sum n\log c$$

$$-\frac{T(\partial(\Delta A))}{\partial T}_V = RT^2\frac{d}{dT}(\log K_c) - \Delta A \quad \text{—(1)}$$

By Gibbs-Helmholtz equation

$$\Delta A = \Delta E + T.\left[\frac{\partial(\Delta A)}{\partial T}\right]_V$$

or $-T\left[\frac{\partial(\Delta A)}{\partial T}\right]_V = \Delta E - \Delta A$ —(2)

By Comparison of equation(1) and(2) we get

$$\Delta E = RT^2\frac{d}{dT}(\log K_c)$$

$$\frac{\Delta E}{RT^2} = \frac{d}{dT}(\log K_c)$$

But $\Delta E = q_V$ where q_V is the heat absorbed by the system at Constant Volume. Hence $\frac{d}{dT}(\log K_c) = \frac{q_V}{RT^2}$

This is the van't Hoff's reaction isochore equation.