

The Relationship between the Equilibrium constant and the Temperature of a Reaction: The Van't Hoff Isochore and the Clausius - Clapeyron Equation.

if $\Delta G = -RT \ln K_p$

is differentiated with respect to temperature at constant pressure

$$\left(\frac{\partial(\Delta G)}{\partial T}\right)_P = -R \ln K_p - RT \left(\frac{\partial \ln K_p}{\partial T}\right)_P$$

multiplying through by T.

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

But the Gibbs - Helmholtz equation state that

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

if the reactants and products are in their standard states.

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

and we can substitute in the equation above.

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

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

and $\frac{d \ln K_p}{dT} = \frac{\Delta H}{RT^2}$ which is known as van't Hoff's isochore

and shows the effect of temperature on the equilibrium constant of a reaction. "isochore" means equal volume, so that this is misleading it stems from van't Hoff's original deduction which was for constant volume.

* Integrating $\Rightarrow \ln K_p = -\frac{\Delta H}{RT} + \text{const}$

So that if we know K_p at one temp. and ΔH , we can calculate K_p at another temp.

the error introduced into the calculated value of K_p (14) is small, if the temperature coefficient of the equilibrium constant is known, this equation allows a calculation of ΔH° .

If we have an exothermic reaction, ΔH° will be negative and therefore K_p will decrease as the temperature increases. For an endothermic reaction K_p will increase as the temperature increases.

⑥ if we consider the vaporization of a liquid A

$A_L = A_G$; ΔH° for this reaction is the latent heat of evaporation of A; The equilibrium constant for this reaction will be $K_p = P_A^\circ$ because the liquid will be in its standard state; P_A° is the vapour pressure of pure liquid A and

$$\left\{ \frac{d \ln P_A^\circ}{dT} = \frac{L_e}{RT^2} \right\} \text{ which is known as Clausius - Clapeyron equation}$$

This equation can be used to calculate (L_e) by measuring the vapour pressure of a substance at various temperature and is important in vacuum metallurgy where the vapour pressure of certain elements can be high enough to cause serious evaporation losses in vacuum melting and casting.

Ex The latent heat of evaporation of manganese at its boiling point (2095°C) is 226 kJ/mol . We can therefore calculate its vapour pressure at the temperature of molten steel (1600°C) using the integrated form of

$$\ln P_{1873}^\circ - \ln P_{2368}^\circ = - \frac{L_e}{R} \left(\frac{1}{1873} - \frac{1}{2368} \right)$$

$P_{2368}^\circ = 1 \text{ atm}$, as 2368 K is the boiling point of Manganese.

$$\therefore \ln P_{1873}^\circ = - \left[\frac{226,000}{8.314} \left(\frac{1}{1873} - \frac{1}{2368} \right) \right]$$

$$= -3.04$$

$$\therefore P_{1873}^\circ = 0.048 \text{ atm.}$$

* The Clausius - Clapeyron equation can be extended to cover Sublimation of A.

$$A_s = A_g$$

$$\frac{d \ln P_s^\circ}{dT} = \frac{L_s}{RT^2}$$

where L_s is the latent heat of

Sublimation (per mole) of A; P_s° is the vapour pressure of the pure solid A in contrast with P_A° the vapour pressure of pure liquid A. if the liquid is supercooled to a temperature T, at which the solid is stable, subtracting

$$\frac{d \ln (P_s^\circ / P_A^\circ)}{dT} = \frac{L_s - L_e}{RT^2} = \frac{L_f}{RT^2}$$

where L_f is the latent heat of fusion of A.

If A is a component of a liquid solution, whose solute is insoluble in solid A, at the liquidus temperature of that solution (the temperature at which solid A first appears under equilibrium conditions) then the value of P_s° will be the vapour pressure of solution of A at that temperature. Then $P_s^\circ / P_A^\circ = X_A$ the mole fraction of A in the liquid solution and

$$\frac{d \ln X_A}{dT} = \frac{L_f}{RT^2}$$

when $X_A = 1$ (pure A), the liquidus temperature is the freezing point of pure A, T_f , so that we can integrate between T_f and T_L liquidus temperature of the solution

$$\ln X_A = -\frac{L_f}{R} \left(\frac{1}{T_L} - \frac{1}{T_f} \right)$$

This equation can be used to calculate T_L - the liquidus temperature of the solution and hence $T_f - T_L$ the depression of the freezing point of A.

* This application is only valid if there is no appreciable solid solubility such as is found in the systems Cd-Zn, Cd-Bi. This equation can also be used to calculate L_f , knowing values of T_L and T_f .