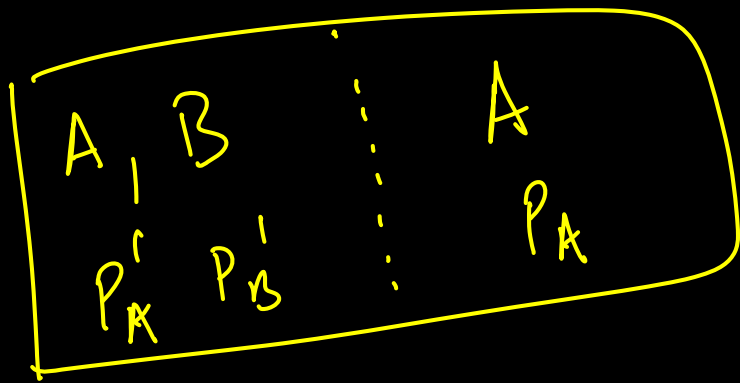


$$\mu_A(\text{mix}, T, P) < \mu_A(\text{pure}, T, P)$$



At equilibrium

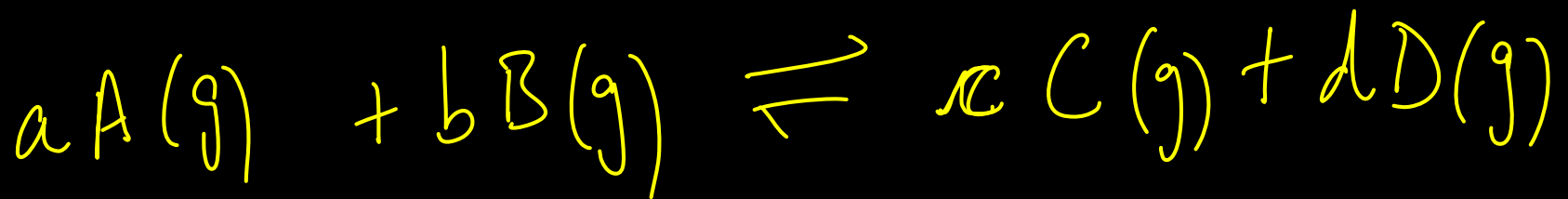
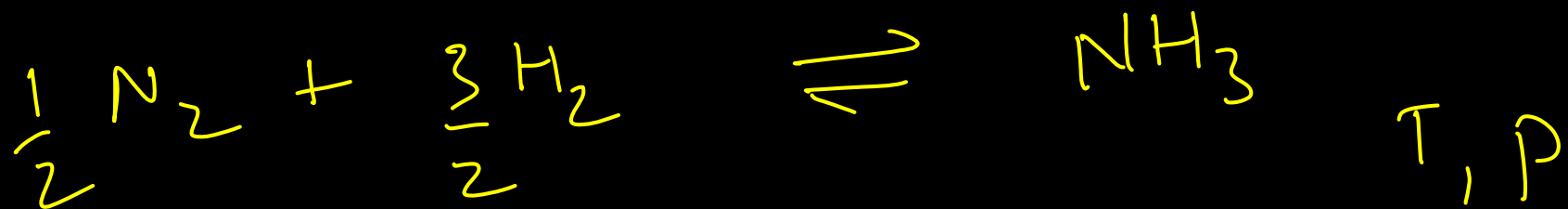
$$\mu_A(\text{mix}, T, P_T) = \mu_A(\text{pure}, T, P_A)$$

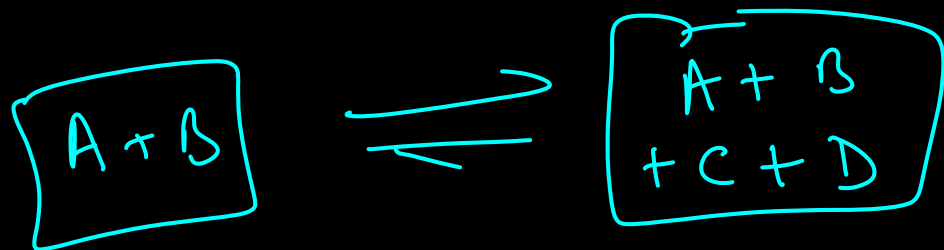
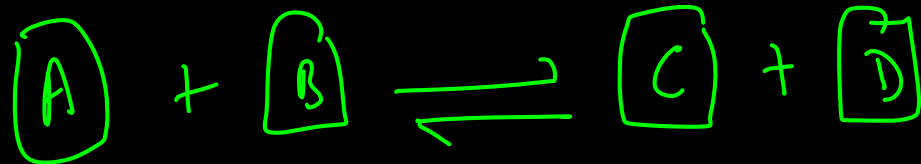
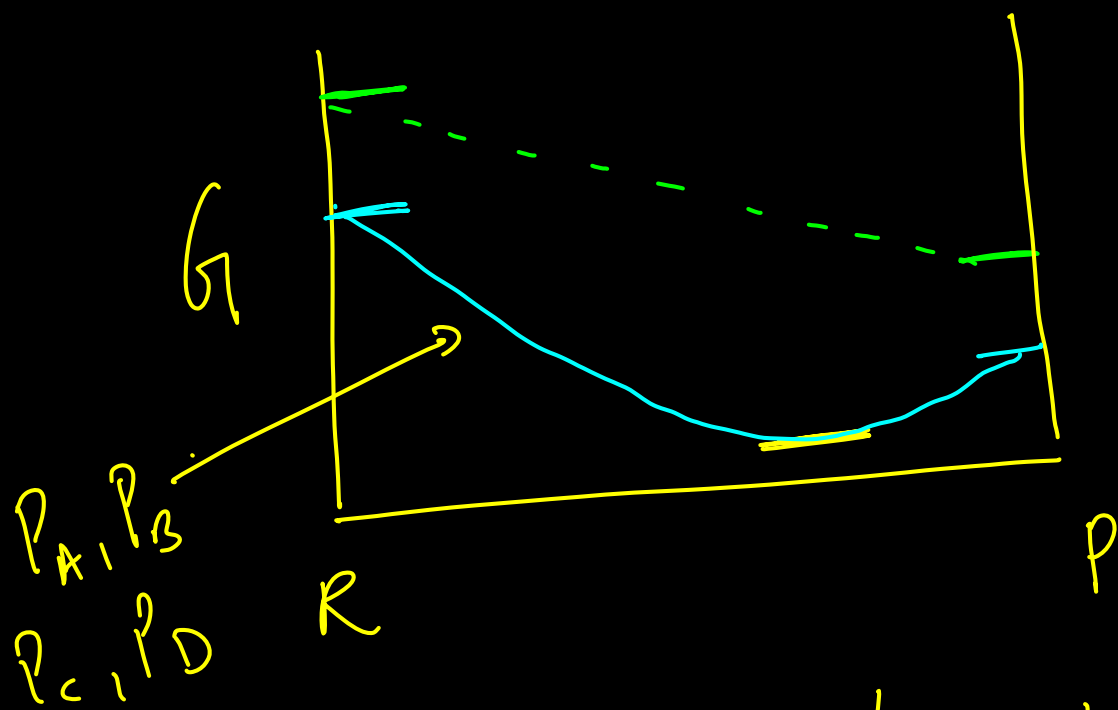
$$= \mu_A(\text{pure}, T, x_A P_T)$$

$$= \mu_A^\ominus(T) + RT \ln(x_A P_T)$$

$$= \underbrace{\mu_A^\ominus(T)} + RT \ln P_T + RT \ln x_A$$

$$\mu_A(\text{mix}, T, P_T) = \mu_A(\text{pure}, T, P_T) + RT \ln x_A$$





$$G_1 = a\mu_A + b\mu_B + c\mu_C + d\mu_D$$

$$G_2 = (a - \varepsilon a)\mu_A + (b - \varepsilon b)\mu_B + (c + \varepsilon c)\mu_C + (d + \varepsilon d)\mu_D$$

$$\Delta G(\varepsilon) = \varepsilon \left[c\mu_C + d\mu_D - (a\mu_A + b\mu_B) \right]$$

$$\left(\frac{\partial G}{\partial p}\right)_T \rightarrow \mu(T) = \mu^\circ(T) + RT \ln p/p^\circ$$

$$\Delta G(E) = \varepsilon \left[c\mu_c^\circ + d\mu_D^\circ - (a\mu_A^\circ + b\mu_B^\circ) + RT \ln \frac{P_c^c P_D^d}{P_A^a P_B^b} \right]$$

$$\Delta G = \Delta G_{rxn}^\circ + RT \ln Q$$

reaction quotient Q

At eq.

$$\Delta G_{rxn}^\circ = -RT \ln Q_{eq.}$$

$$Q_{eq} = K_p$$

$$\Delta G_{rxn}^{\ominus} = -RT \ln K_p$$

$$K_p = e^{-\frac{\Delta G_{rxn}^{\ominus}}{RT}}$$

$$K_p = \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

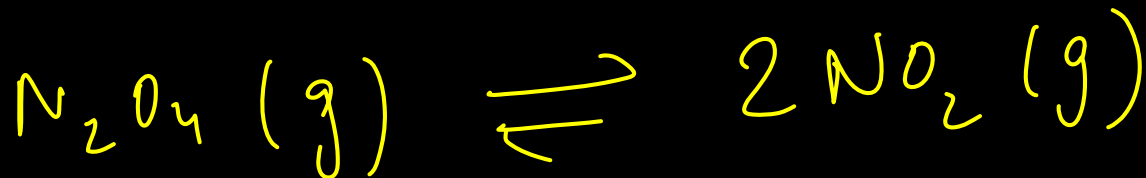
$$= P_T^{c+d-a-b}$$

$$= P^{\Delta \nu}$$

$$K_X$$

$$\frac{X_C^c X_D^d}{X_A^a X_B^b}$$

$$K_x = p^{-\Delta v} K_p$$



initial

n

0

at eq.

$n-x$

$2x$

$\frac{n-x}{n+x}$

$\frac{2x}{n+x}$

$$K_p = \frac{p_{\text{NO}_2}^2}{p_{\text{N}_2\text{O}_4}} \approx p \frac{X_{\text{NO}_2}^2}{X_{\text{N}_2\text{O}_4}} = p \frac{4x^2}{n^2 - x^2}$$

Extent of reaction = $\alpha = x/n$

$$K_p = P \frac{4\alpha^2}{1-\alpha^2}$$

$$\alpha = \left[1 + \frac{4P}{K_p} \right]^{-1/2}$$

Le Chatelier's principle for pressure

$$\ln K_p(T) = - \frac{\Delta G^\ominus}{RT}$$

$$\frac{d \ln K}{dT} = \frac{d \left(- \frac{\Delta G^\ominus}{RT} \right)}{dT} = \frac{\Delta G^\ominus}{RT^2} - \frac{1}{RT} \frac{d \Delta G^\ominus}{dT}$$

$$\left(\frac{\partial \Delta G^\ominus}{\partial T} \right)_{p=1 \text{ bar}} = - \Delta S^\ominus(T)$$

$$\frac{\Delta H^\ominus - T \Delta S^\ominus}{RT^2} + \frac{1}{RT} \Delta S^\ominus$$

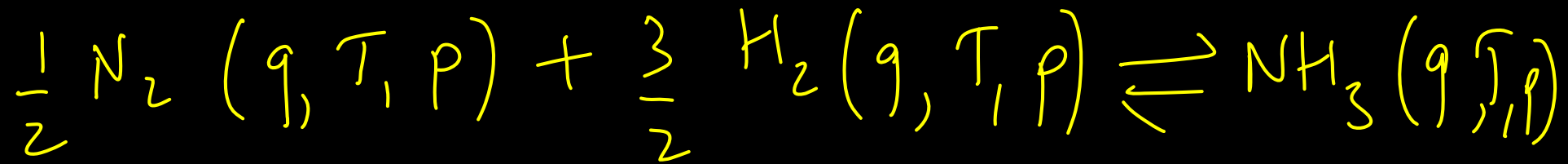
$$\frac{d \ln K}{dT} = \frac{\Delta H^\ominus}{RT^2}$$

van't Hoff
equation

$$\ln K_2 - \ln K_1 = \int_{T_1}^{T_2} \frac{\Delta H^\ominus}{RT^2} dT$$

$$\Delta H^\ominus(T_2) = \Delta H^\ominus(T_1) + \Delta C_p (T_2 - T_1)$$

$$\ln K_2 = \ln K_1 + \frac{\Delta H^\ominus}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$



$$\Delta H_{\text{rxn}}^{\ominus} (298 \text{ K}) = -46.21 \text{ kJ mol}^{-1}$$

$$\Delta G_{\text{rxn}}^{\ominus} (298 \text{ K}) = -16.74 \text{ kJ mol}^{-1}$$

$$K_p = \frac{P_{\text{NH}_3}}{P_{\text{H}_2}^{3/2} P_{\text{N}_2}^{1/2}} = P^{-1} \frac{X_{\text{NH}_3}}{X_{\text{H}_2}^{3/2} X_{\text{N}_2}^{1/2}} = e^{-\Delta G^{\ominus}/RT} = 860$$

$$800 \text{ K} \rightarrow K_p = 0.007$$

$$K_x = p K_p$$

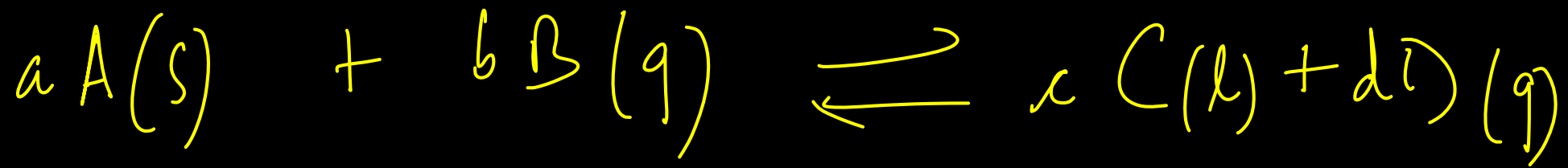
$$100 \text{ bar} \quad K_x = 0.7$$

Gerhard Ertl

$$\mu_A(T, P, C_A) = \mu_A^\ominus(T, P) + RT \ln \frac{C_A}{\text{std. conc.}}$$

[A]

$$K_{eq} = K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$



$$\Delta G = c\mu_c^\circ + d\mu_D^\circ - a\mu_A^\circ - b\mu_B^\circ + RT \ln \frac{P_D^d}{P_B^b}$$

$$\Delta G_{rxn}^\circ + RT \ln Q_{eq}$$