

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

AT CONSTANT T

$$dG = -SdT + VdP$$

$$G(T, P) - G(T, P^0) = \int_{P^0}^P V dP$$

FOR SOLIDS AND LIQUIDS

$$G(T, P) \cong G(T, P^0) + V(P - P^0)$$

FOR GASES

IDEAL

$$G(T, P) \cong G(T, P^0) + \int_{P^0}^P \frac{nRT}{P'} dP'$$

$$G(T, P) = G(T, P^c) + nRT \ln\left(\frac{P}{P^c}\right) \quad \boxed{T \text{ const}}$$

$$\left(\frac{\partial G/T}{\partial T}\right)_P = \frac{1}{T} \left(\frac{\partial G}{\partial T}\right)_P - \frac{1}{T^2} G$$

$$= -\frac{S}{T} - \frac{G}{T^2} = -\frac{G + TS}{T^2}$$

$$= -\frac{H}{T^2}$$

$$d\left(\frac{\Delta G}{T}\right) = -\Delta H \frac{dT}{T^2} \approx + d\left(\frac{\Delta H}{T}\right)$$

$\Delta H$  TEMP INDEPENDENT

$$\frac{\Delta G(T_2)}{T_2} - \frac{\Delta G(T_1)}{T_1} = \Delta H(T_1) \left[ \frac{1}{T_2} - \frac{1}{T_1} \right]$$

## CHEMICAL RXN

$$G(T, P, n_1, n_2, \dots, n_N)$$

$$dG = \left( \frac{\partial G}{\partial T} \right)_{P, n_1, n_2, \dots, n_N} dT + \left( \frac{\partial G}{\partial P} \right)_{T, n_1, n_2, \dots, n_N} dP$$

$$+ \left( \frac{\partial G}{\partial n_1} \right)_{T, P, n_2, \dots, n_N} dn_1 + \left( \frac{\partial G}{\partial n_2} \right)_{T, P, n_1, n_3, \dots, n_N} dn_2 + \dots +$$

$$\left( \frac{\partial G}{\partial n_N} \right)_{T, P, n_1, n_2, \dots, n_{N-1}} dn_N$$

## DEF CHEMICAL POTENTIAL

$$\mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{T, P, n_j, \dots, n_N} \quad n_j \neq n_i$$

$$dG = \left( \frac{\partial G}{\partial T} \right)_{P, n_1, n_2, \dots, n_N} dT + \left( \frac{\partial G}{\partial P} \right)_{T, n_1, \dots, n_N} dP + \sum_i \mu_i dn_i$$

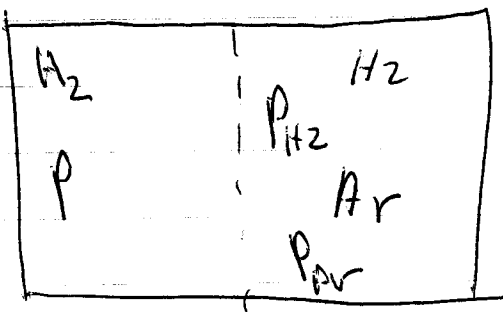
AT CONSTANT (T, P)

$$dG = \sum_i \mu_i dn_i$$

$$\int_0^G dG' = G = \sum_i \int_0^{n_i} \mu_i dn_i$$

$$G = \sum_i n_i \mu_i$$

$\mu_i$  is the molar Gibbs energy



$$\mu_{H_2}^{\text{PURE}} = \mu_{H_2}^{\text{MIX}}$$

FOR AN IDEAL GAS

$$\mu_{H_2}^{\text{PURE}}(T, P) = \mu_{H_2}^{\circ}(T, P^{\circ}) + RT \ln\left(\frac{P_{H_2}}{P^{\circ}}\right) = \mu_{H_2}^{\text{MIX}}(T, P)$$

BOT

$$P_{H_2}^L = P_{H_2}^R = X_{H_2} P$$

$$\mu_{H_2}^{MIX}(T, P) = \mu_{H_2}^0(T, P^0) + RT \ln\left(\frac{P}{P^0}\right) + RT \ln X_{H_2}$$

$$\mu_{H_2}^{MIX}(T, P) = \mu_{H_2}^{PURE}(T, P) + RT \ln X_{H_2}$$

IN THE CASE OF FOUR GASES  $X_{He}, Ar, Ne, He$

INITIAL CONDITION BEFORE MIXING

$$G_i = n_{He} \mu_{He}^{PURE} + n_{Ne} \mu_{Ne}^{PURE} + n_{Ar} \mu_{Ar}^{PURE} + n_{Xe} \mu_{Xe}^{PURE}$$

$$G_f = n_{He} \mu_{He}^{MIX} + n_{Ne} \mu_{Ne}^{MIX} + n_{Ar} \mu_{Ar}^{MIX} + n_{Xe} \mu_{Xe}^{MIX}$$

$$\Delta G_{\text{mix}} \equiv G_f - G_i$$

$$\Delta G_{\text{mix}} = RT \sum_i n_i \ln X_i < 0$$

$$X_i < 1$$

MIXING IS AN SPONTANEOUS PROCESS

$$\rightarrow \left( \frac{\partial \Delta G_{\text{mix}}}{\partial T} \right)_p = \Delta S_{\text{mix}} = -R \sum_i n_i \ln X_i > 0$$

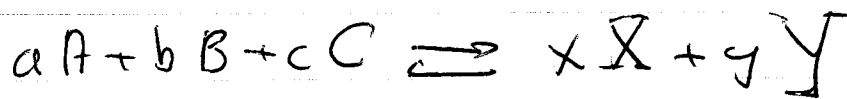
$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T \Delta S_{\text{mix}}$$

FOR IDEAL GASES OR IDEAL SOLUTIONS

$$\Delta G_{\text{mix}} = -T \Delta S_{\text{mix}}$$

$$\Rightarrow \Delta H_{\text{mix}} = 0$$

## CHEMICAL RXN



AN INFINITESIMAL CHANGE  $\Rightarrow$

$$dG = \sum_i \mu_i dn_i$$

LET US DEFINE THE EXTENT OF REACTION

$\xi$  AS

$$n_i = n_i^{\text{INITIAL}} + \nu_i \xi$$

$$dn_i = \nu_i d\xi$$

$$\Rightarrow dG = \left( \sum_i \nu_i \mu_i \right) d\xi$$

$$\left( \frac{\partial G}{\partial \xi} \right)_{T,P} = \sum_i \nu_i \mu_i \equiv \Delta G_{\text{rxn}}$$

REMEMBER THAT

$$\mu_i^{\text{MIX}}(T, P) = \mu_i^{\text{MO}}(T, P^0) + RT \ln \left( \frac{P_i}{P^0} \right)$$

$$\Delta G_{rxn} = \sum_i \nu_i \mu_i(T, p_i) + \sum_i \nu_i RT \ln \left( \frac{p_i}{p^0} \right)$$

$$\Delta G_{rxn} \equiv \Delta G_{rxn}^{\circ} + \sum_i \nu_i RT \ln \left( \frac{p_i}{p^0} \right)$$

SINCE WE ONLY NEED  $\Delta G_{rxn}^{\circ}$

WE CAN PICK ANY "ZERO" POINT AND

DEFINE  $\Delta G_f^{\circ}(T, p^0)$

WHICH, AS IN THE CASE OF  $\Delta H_f^{\circ}$ , IS

ZERO FOR THE ELEMENTS AT ITS  
STANDARD STATE.

$$\Delta G_{rxn}^{\circ} = \sum_i \nu_i \Delta G_f^{\circ}[i]$$

$$\Delta G_{rxn} = \Delta G_{rxn}^{\circ} + RT \sum_i \nu_i \ln \left( \frac{p_i}{p^0} \right)$$

$$\Delta G_{rxn} = \Delta G_{rxn}^{\circ} + RT \sum_i \ln \left( \frac{p_i}{p^0} \right)^{\nu_i}$$





$$\Delta G_{\text{rxn}} = x\mu_X + y\mu_Y - a\mu_A - b\mu_B$$

$$= x\mu_X^0 + y\mu_Y^0 - a\mu_A^0 - b\mu_B^0$$

$$+ xRT \ln\left(\frac{P_X}{p^0}\right) + yRT \ln\left(\frac{P_Y}{p^0}\right)$$

$$- aRT \ln\left(\frac{P_A}{p^0}\right) - bRT \ln\left(\frac{P_B}{p^0}\right)$$

$$= \sum_c \nu_c \mu_c^0 + RT \ln \left\{ \frac{\left(\frac{P_X}{p^0}\right)^x \left(\frac{P_Y}{p^0}\right)^y}{\left(\frac{P_A}{p^0}\right)^a \left(\frac{P_B}{p^0}\right)^b} \right\}$$

$$\boxed{\Delta G_{\text{rxn}} \equiv \Delta G_{\text{rxn}}^0 + RT \ln Q}$$

At EQUILIBRIUM

$$\Delta G_{\text{rxn}} = 0$$

$$0 \equiv \Delta G_{\text{rxn}}^0 + RT \ln K_p$$

$$P_i = X_i P_T \quad \Rightarrow \quad \frac{P_i}{p^0} = X_i \frac{P_T}{p^0}$$

$$K_p \equiv \frac{\left(\frac{p_x^{\text{eq}}}{p^0}\right)^x \left(\frac{p_y^{\text{eq}}}{p^0}\right)^y}{\left(\frac{p_A^{\text{eq}}}{p^0}\right)^a \left(\frac{p_B^{\text{eq}}}{p^0}\right)^b}$$

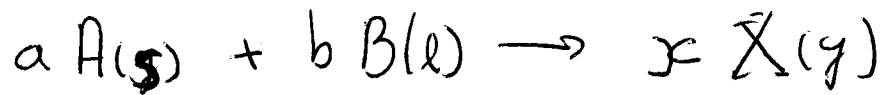
$$= \frac{X_X^x X_Y^y}{X_A^a X_B^b} \left(\frac{P_T}{p^0}\right)^{x+y-a-b}$$

$$K_p = K_x \left(\frac{P_T}{p^0}\right)^{\Delta \nu}$$

$$pV = nRT$$

$$\frac{p}{p^0} = \frac{n}{V} \frac{RT}{p^0} = \frac{C_i}{C^0} \frac{C^0 RT}{p^0}$$

$$K_p = K_c \left(\frac{C^0 RT}{p^0}\right)^{\Delta \nu}$$



$$\Delta G_{\text{rxn}} = x \mu_X - a \mu_A - b \mu_B$$

$$\mu_X = \mu_X^0 + RT \ln \left( \frac{p_X}{p^0} \right)$$

$$\mu_A \approx \mu_A^0$$

$$\mu_B \approx \mu_B^0$$

$$\Delta G_{\text{rxn}} = \Delta G_{\text{rxn}}^0 + RT \ln \left( \frac{p_X}{p^0} \right)^x$$

$$0 = -RT \ln K_p + RT \ln \left( \frac{p_X}{p^0} \right)^x$$

$$\ln K_p = \ln \left( \frac{p_X}{p^0} \right)^x$$

$$K_p = \left( \frac{p_X}{p^0} \right)^x$$