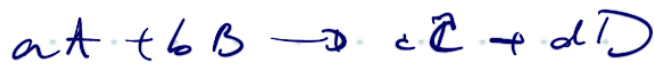


Ch 9 Chemical Thermodynamics

Reactions - homogeneous - one phase

heterogeneous - multiple phases



law of mass action - thermodynamic eq. concentrations

↓
does not depend on initial conditions

eq. condition: $G = \text{minimized @ } T \text{ \& } p \text{ constant}$

- ΔH°
- given temp [≠] → strong temp-dependence but ΔH° has weaker temp dependence
 - standard pressure (1 bar = 1.01 atm) → weak press effect
 - unmixed reactants and products

note: not free case for ΔG°

"enthalpy change of reaction" / "heat of reaction"

$\Delta H^\circ > 0 \Rightarrow$ endothermic

$\Delta H^\circ < 0 \Rightarrow$ exothermic

$$\Delta H^\circ(T) = \Delta H^\circ_{ref} + \Delta C_p (T - T_{ref})$$
$$\Delta C_p = (dC_{pD} + cC_{pC}) - (aC_{pA} + bC_{pB})$$

assuming linear,

$$h_i^\circ(T) = h_{i,ref}^\circ + C_{p,i} (T - T_{ref})$$

Entropy change of reaction

$$\Delta S^\circ = S^\circ(\text{products}) - S^\circ(\text{reactants})$$

$$S_i^\circ(T) = S_i^{\circ \text{ref}} + C_{p,i} \ln \frac{T}{T_{\text{ref}}}$$

$$\Rightarrow \Delta S^\circ(T) = \Delta S_{\text{ref}}^\circ + \Delta C_p \ln \left(\frac{T}{T_{\text{ref}}} \right)$$

gas translation & rotation

$$\text{eg: } M = 32 \quad T = 300\text{K} \Rightarrow S^\circ = 160 \text{ J/mol}\cdot\text{K}$$

$$R \approx 8.3 \text{ J/mol}\cdot\text{K}$$

dominates \Rightarrow most ideal gases: $S^\circ(T) = R \left[\ln \left(M^{3/2} T^{5/2} \right) - 1.92 \right]$

$M =$ Molecular weight of gas

solids 3rd law of thermod: $S(T=0) = 0$

$$\Rightarrow S^\circ = \int_0^T C_p(T') / T' dt'$$

note: gas entropy dominates over condensed-phase entropy

Entropy rule of thumb: 200 J/mole-K for gas species,
and ignore the condensed phases

Criterion of Equilibrium

$$dG = 0 = \sum_i \mu_i dn_i$$

$$\Rightarrow dn_D = \left(\frac{c}{a}\right) dn_A, \quad dn_C = \left(-\frac{c}{a}\right) dn_A, \quad dn_D = \frac{d}{a} dn_A$$

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

generally,

$$\sum_{\text{products}} \nu_i \mu_i = \sum_{\text{reactants}} \nu_j \mu_j \quad (1)$$

law of mass action

$$\mu_i = g_i^\circ + RT \ln a_i \quad (2)$$

$$\textcircled{1}, \textcircled{2} \Rightarrow \Delta G^\circ + RT \ln \left(\frac{a_C^c a_D^d}{a_A^a a_B^b} \right) = 0$$

Equilibrium constant:

$$K = \frac{a_C^c a_D^d}{a_A^a a_B^b} = e^{-\Delta G^\circ / RT}$$

when $\gamma_i = 1 \Rightarrow$

$$K \rightarrow \frac{\gamma_C^c \gamma_D^d}{\gamma_A^a \gamma_B^b}$$

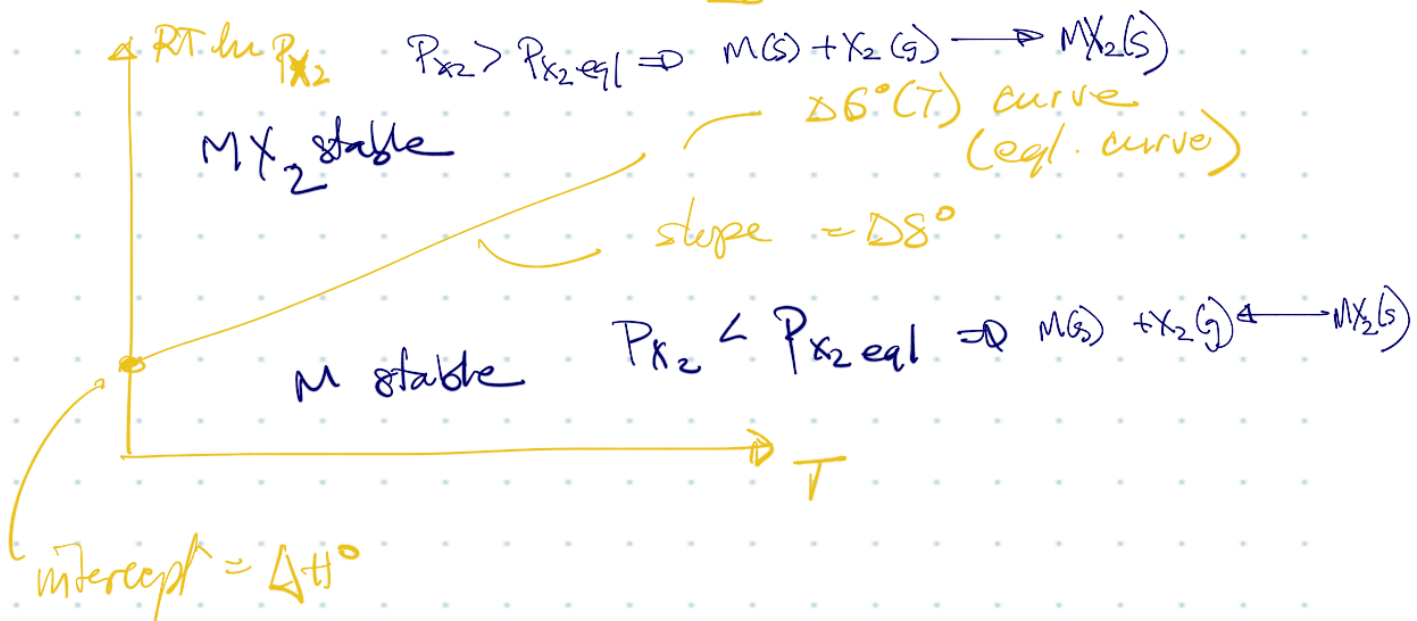
reaction progress variable ξ arbitrary \rightarrow there is only one degree of freedom for the compositions, so assign ξ to one of the concentrations & then solve for it.

Stability Diagrams

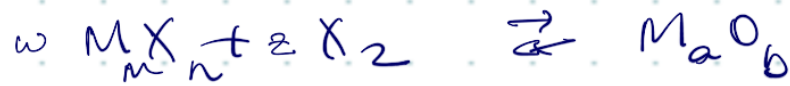


assume immiscible

$$\Rightarrow RT \ln P_0 = \Delta G^\circ = G_{MX_2}^\circ - G_{O_2}^\circ - G_M^\circ \\ \approx \Delta H^\circ - T\Delta S^\circ$$



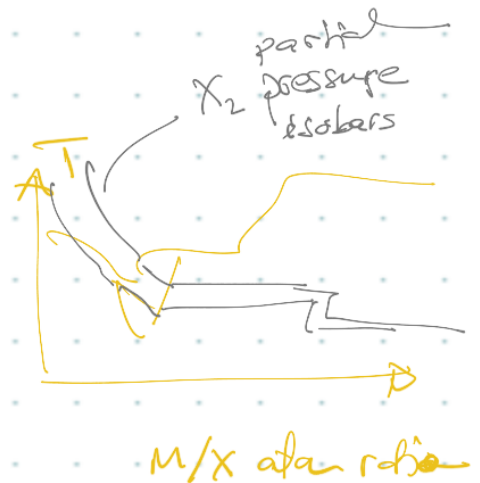
Reactive Gas Isobars on a Phase Diagram



$$P_{X_2} = e^{\Delta G^\circ / 2RT}$$

$$z = (b - a \cdot n/m) / 2$$

↓
composition on the phase diagram



Reactions Involving Solutions

$$\mu_i = g_i^\circ + RT \ln a_i$$



$$\Delta G^\circ_M$$



$$\Delta G^\circ_P$$



assume ideal solutions

$$K_M = e^{-\Delta G^\circ_M / RT} = \frac{X_{MX_2}^{\text{slag}}}{X_M^{\text{melt}} P_{X_2}}$$

$$K_P = e^{-\Delta G^\circ_P / RT} = \frac{X_{PX_2}^{\text{slag}}}{X_P^{\text{melt}} P_{X_2}}$$

$$\Rightarrow \frac{K_M}{K_P} = \frac{X_{MX_2}^{\text{slag}} X_P^{\text{melt}}}{X_{PX_2}^{\text{slag}} X_M^{\text{melt}}}$$



Assume fixed: $\begin{cases} \mu/P = 1 \\ \sigma/P = 2 \end{cases} \rightarrow$ no O_2 exchange with surroundings
(closed system)

"reaction progress variable"

let $\xi \equiv$ mol $M_{O_2} =$ mol P @ eq.

$\&$

$1 - \xi =$ mol $M_{O_2} =$ mol M @ eq.

$$\Rightarrow \frac{K_m}{K_p} = \frac{e^{-\Delta G_m^\circ/RT}}{e^{-\Delta G_p^\circ/RT}} = e^{-(\Delta G_m^\circ - \Delta G_p^\circ)/RT} = \frac{\xi^2}{(1-\xi)^2}$$

$$K_p = \frac{(1-\xi)}{\xi p_{O_2}}$$

Thermochemical Databases

Standard free energy of formation
↓
formation reactions

"Ellingham Diagrams"

$\Delta G^\circ(T)$

↓
per mol F_2 → to permit comparison
among MF_n compounds

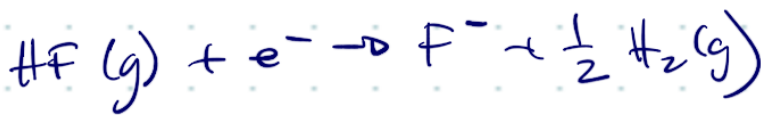
Presentation of Data of Equilibria in molten Halides



$$K = \frac{a_{MF_n} f_{HF}}{a_{MF_{n+1}} f_{H_2}^{1/2}} = \frac{X_{MF_n} \gamma_{MF_n} P_{HF}}{X_{MF_{n+1}} \gamma_{MF_{n+1}} P_{H_2}^{1/2}} = Q \frac{\gamma_{MF_n}}{\gamma_{MF_{n+1}}}$$

$$\Delta G_r = -RT \ln K = \boxed{-RT \ln Q} - RT \ln \frac{\gamma_{MF_n}}{\gamma_{MF_{n+1}}}$$

$$\boxed{\Delta G^\circ = -nFE^\circ}$$



reference half-cell reaction



$$E^\circ = 0$$

$$\Delta G^\circ = 0$$



$$\log K = a + b \left(\frac{10000}{T} \right)$$

obtained from $\ln K(T)$ plots

strongly covariant \Rightarrow large errors when used to calculate ΔH & ΔS



Ellingham diagram: $RT \ln \left(P_{F_2}^{n/2} \right)$ vs T



Ellingham diagram: $RT \ln \left(P_{HF} / P_{H_2}^{n/2} \right)$ vs T



Ellingham diagram: $RT \ln \left(P_{O_2}^{n/4} \right)$ vs T

limitation of Ellingham diagram:

cannot simultaneously show all possible reactions.

Pourbaix diagrams

"chemical phase diagrams"

- ↓
- note: only useful for compounds that are already known and characterized

↓

cannot predict formation of new species or compounds

reference half cell reaction choice $\Rightarrow \log (P_{\text{HF}} / P_{\text{H}_2}^{(2)})$ y axis

$\log X_{\text{O}_2}$ x axis

other options: $\log P_{\text{H}_2}$, $\log (X_{\text{U}^{4+}} / X_{\text{U}^{3+}})$

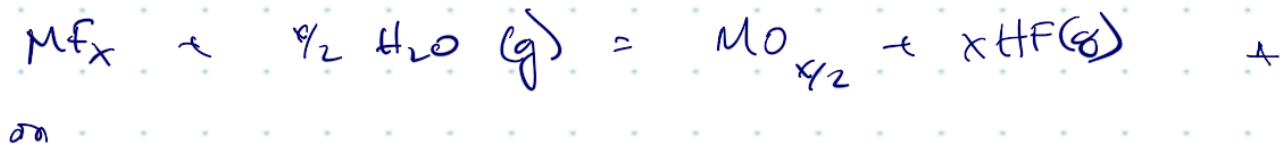
any redox couple may be used

example: M^0 , M^+ , M^{2+} oxidation states

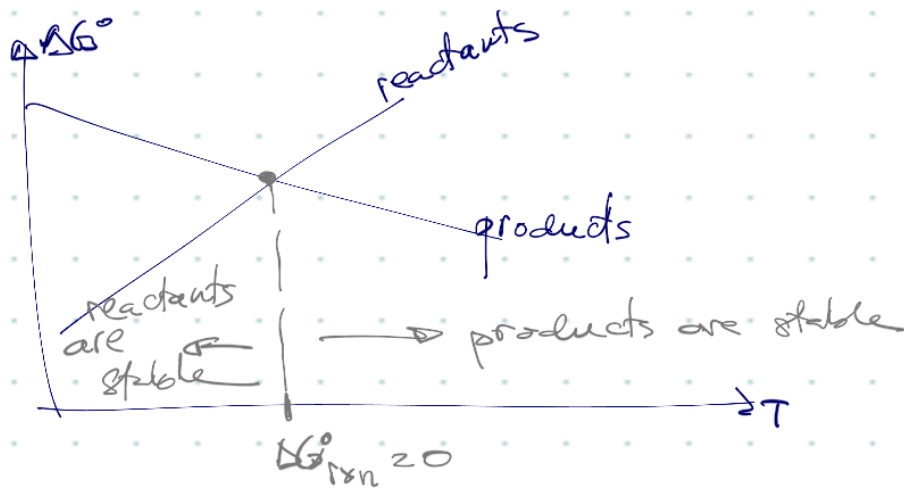
fluoride & oxide species

Hydrolysis temperature

(Article: Materials Today, 2010 Vol. 13 (12))



$$\Delta G_A = x \Delta G_{HF}(T) + \Delta G_{MO_{\frac{x}{2}}}(T) - \frac{1}{2} \Delta G_{H_2O}(T) - \Delta G_{MF_x}(T)$$



Salt preparation temp < hydrolysis temp

↓
 solution \Rightarrow increases MF_x stability & reduces amount of hydrolysis that occurs

- traces of water are not stable in molten fluorides \Rightarrow either vapor escapes, or it reacts

- HF \rightarrow high solubility in molten salts



subsequently oxidizes metals

- HF (H₂ (g)) sparging \rightarrow ratio sets the redox potential

- Vacuum drying prior to melting

10^{-5} torr $400 - 425^\circ\text{C}$

Redox condition in molten fluorides

↓
related to μ of F^- (the anion species)

↕
related to m/m^+

↓
defined in terms of
 P_{F_2}

$$\overline{\Delta G_{x_2}} \equiv RT \ln P_{x_2}$$

H_2/HF

Be addition

CeF_3/CeF_4