Chap.19. Reactions involving Gases

Every one who drinks this water will thirsty again, but whoever drinks the water I give him will never thirst.

(요 4:1)

19.1. Intro.

one extreme → perfect gas : no interactive forces among the particles.
no heat effects. during mixing.

the other → Other extreme : chemical affinity. heat of mixing (yes).

$$\Delta G = \Delta G \text{ due to chemical rxn}$$

$$+ \Delta G \text{ due to the mixing of the appearing } p$$
w/ the remaining reactant gases.

(Knowledge about ΔG w/ comp.
(unmixed. reactant. product. gases)

19.2. Rxn Equil^m in a (gas) (mixture) & (Equil^m) (Const.)

- For the rxn $A_{(g)} + B_{(g)} = 2 C_{(g)}$ at const T. P.

(9.1) At any moment $G' = n_A \bar{G}_A + n_B \bar{G}_B + n_C \bar{G}_C$ — partial m free E.

n_A, n_B. n_C will be determined to minimize $\underline{G'}$.

if $n_A = n_B = 1$ mole as starting gases. , 1 mole of each will produce 2 moles of C.

At any time $n_A = n_B$ $n_C = 2 - n_A - n_B = 2(1 - n_A)$.

$$\therefore G' = n_A \bar{G}_A + n_A \bar{G}_B + 2(1 - n_A) \bar{G}_C. = f(n_A, \bar{G}_i).$$

(8.15) $\bar{G}_i = G_i^\circ + RT \ln P + RT \ln X_i.$

$$X_A = \frac{n_A}{2} , \quad X_B = \frac{n_B}{2} \quad X_C = \frac{2(1-n_A)}{2} = 1 - n_A.$$

$$\therefore G' = n_A (G_A^° + G_B^° - 2G_c^°) + 2G_c^° + 2RT\ln P + 2RT\left[n_A \ln\left(\frac{n_A}{2}\right)\right.$$
$$\left. + (1-n_A)\ln(1-n_A)\right]$$

(9.2) $\therefore G' - 2G_c^° = n_A\left[-\Delta G^°\right] + 2RT\ln P + 2RT\left[n_A \ln\left(\frac{n_A}{2}\right)\right.$

the standard free E. change for the at

$$\left. + (1-n_A)\ln(1-n_A)\right]$$

if total Pressure $=1$. $RT\ln P = 0$.

(9.2) → (9.3) $G' - 2G_c^° = \underbrace{n_A\left[-\Delta G^°\right]}_{\text{Chemical}} + 2RT\left[n_A\ln\left(\frac{n_A}{2}\right) + (1-n_A)\right.$

not initial
anytime

the difference bet'n the f.E of the 2 mole sys. $(n_A = n_A)$

& the f.E. of the system when it consists of 2 m.

Look at the Text.   (Fig. 9.1) p 226 - 227.

for the example. $A_{(g)} + B_{(g)} = 2C_{(g)}$ mixing.

Curve I = line II + Curve III $G_A^° + G_B^° = 0$ 이라고

chem. rxn.   gas mixing $2G_c^° = -5000 J$

min. free Energy ⇒ the equil^m state. $R[n_A\ln\frac{}{}$

$\ln\frac{}{}$

⇒ for the equil^n Criterion. $\left(\frac{\partial G'}{\partial n_A}\right)_{T.P} = 0$. $= -5763 J$

Since $G' = n_A \bar{G}_A + n_A \bar{G}_B + 2(1-n_A)\bar{G}_c$

$$\left(\frac{\partial G'}{\partial n_A}\right)_{T.P} = \bar{G}_A + \bar{G}_B - 2\bar{G}_c = 0 .$$

(9.4) $\boxed{\therefore \text{ the Criterion of rxn equil}^n \quad \bar{G}_A + \bar{G}_B = 2\bar{G}_c}$ ‖

(9.5). (9-4) → $G_A^\circ + RT\ln P_A + G_B^\circ + RT\ln P_B = 2G_C^\circ + 2RT\ln$

∴ $2G_C^\circ - G_A^\circ - G_B^\circ = -RT\ln \dfrac{P_C^2}{P_A P_B}$

(9.6) ⇒ $\Delta G^\circ = -RT\ln\left(\dfrac{P_C^2}{P_A P_B}\right)$ ef. $= -RT$

$\left(\dfrac{P_C^2}{P_A P_B}\right)$ ef $= K_p$, the equil^m const.

정해진 온도에서 equil^m can ↑ 또는 ↓ 가는것

As $\Delta G^\circ = f(T)$ only ⇒ $K_p = f(T)$ only.

$G^\circ = G(T, P=1\,atm)$
$H^\circ = H(T, P=1\,atm)$

10.3 The Effect of Temp. on the $\underline{K_p}$.

The variation of K_p w/ T is from the Gibbs - Helmholtz eq.

$\left[\dfrac{\partial(\Delta G^\circ/T)}{\partial T}\right]_P = -\dfrac{\Delta H^\circ}{T^2}$ as $\Delta G^\circ = -RT\ln K_p$

(14.9), (14.10) $\boxed{\dfrac{\partial \ln K_p}{\partial T} = \dfrac{\Delta H^\circ}{RT^2}}$ → $\left|\dfrac{\partial \ln K_p}{\partial(1/T)} = -\dfrac{\Delta H^\circ}{R}\right|$

Van't Ho

⇒ the effect of T on K_p determined by the sign and the map
if $\Delta H^\circ > 0$ (endo) → $K_p \uparrow$ as $T\uparrow$.
if $\Delta H^\circ < 0$ (exo) → $K_p \downarrow$ as $T\uparrow$.

for $Cl_2 = 2Cl$ rxn. $\Delta H^\circ > 0$. (endo) $K_p = \dfrac{P_{Cl}^2}{P_{Cl_2}}$

more heat (high T) then K_p
to absorb heat (Le chat

(10.10) shows if $\Delta H^\circ \neq f(T)$. $\underline{\ln K_p \text{ varies linearly w/ } 1/T}$

11.

119.4.   The Effect of P on K_p

const $= K_p = \left(\dfrac{P_c^2}{P_A P_B}\right)^{eq.} \pm f(P)$ ← total pressure $\Delta G^0 = -RT \ln K_p$

$\therefore \Delta G^0 = 2 G_c^0 - G_A^0 - G_A^0$ from previous ex. $A + B = 2C$.

$f(P)^* \hookrightarrow$ P.E. diff bet'n pure product. at $P = 1$ atm.!!
                        & pure reactants

But. When K_p is expressed w/ the # of moles of species present. rather than partial pressures. , then K_p is dep on the total pressure ⟨if⟩ the chemical rxn under consideration involves a ⟨change⟩ in the total # of moles present.!!
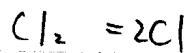
$\xrightarrow{\text{(ex1)}}$ $Cl_2 = 2Cl$ if P increased $\to 2Cl \to Cl_2$

$\xrightarrow{\qquad} Cl_2 \to 2Cl$

$K_p = \left(\dfrac{P_{Cl}^2}{P_{Cl_2}}\right) = \dfrac{(X_{Cl} P)^2}{X_{Cl_2} P} = \boxed{\dfrac{X_{Cl}^2}{X_{Cl_2}} P = K_x P}$ $P \downarrow$

$\hookrightarrow$ indep. of pressure.

K_x changes according to the variation of P.

$K_x \downarrow P \uparrow = K_x \uparrow P \downarrow$

$P \uparrow$ cause decrease in $K_x \dfrac{X_{Cl}^2}{X_{Cl} + X_{Cl}} \to$ shifts react equil^m toward Cl_2 produc

$\xrightarrow{\text{(ex2)}}$ $A + B = 2C$ No change in the # of moles before. after r

$K_p = \dfrac{P_c^2}{P_A P_B} = \dfrac{X_c^2 P^2}{X_A P X_B P} = \dfrac{X_c^2}{X_A X_B} = \underline{\underline{K_x}}$.

if $P \neq 1$ the term $2 RT \ln P$ is eq. (9.2) is raising or lowering the but no change in the position of the min. w.r.t. composition

$\xrightarrow{\qquad}$ $a A + b B = c C + d D$ total pressu

$K_p = K_x P^{c+d-a-b}$ if $d+c-a-b=0 \to K_p = K_x \neq f(P)$
                             K_p and for gaseous phase.

11.5 Reaction Equil^m as a compromise bet'n H & S.

to reduce $G(=H-TS)$, low H. high S (which are contradicting e
                                  required.   Other)

For $Cl_2 = 2Cl$ $\Delta H° > 0$.

$\Delta S° > 0$ ∵ 1 mole → 2 moles

∴ Cl ↑ high H & S | need to be
   Cl_2 ↑ low H & S | compromised.

∴ H & S compromise to have a min G.

ex. $A + B = 2C$.   (11.3)   (2mole sys. $n_A = 1$, $n_B = 1$ initially).

$-\Delta G° = -(\Delta H° - T\Delta S°)$

$G' - 2G_c° = n_A(-\Delta H°) + n_A(T\Delta S°) + 2RT\left[n_A \ln \frac{n_A}{2} + (1-n_A)\ln(1-n_A)\right]$

$= n_A(-\Delta H°) + T\int \underline{n_A \Delta S°} + 2R\left[\underline{\quad\quad\quad^{u}\quad\quad\quad}\right]$

↑   by chem. rxn ↓   gas mixing ↓

enthalpy contribution.   entropy.

11.6.   Rxn Eq^m in $SO_{2(g)} - SO_{3(g)} - O_{2(g)}$.

초기 1 atm.   1 mole   ½ mole   0 $\Delta H° - T\Delta S°$

$SO_{2(g)} + \frac{1}{2}O_{2(g)} = SO_{3(g)}$. $\Delta G° = -94,600 + 89.37 T$.

ex. $\Delta G°_{1000} = -5230 J$ ← $= G°_{SO_3} - \frac{1}{2}G°_{O_2} - G°_{SO_2}$.

평형 1 atm $1-x$ $\frac{1}{2}(1-x)$ x $= -RT\ln K_p$ p=1 at

1.876   ← $K_p = \dfrac{P_{SO_3}}{P_{SO_2} P_{O_2}^{1/2}}$ at 1000K

$n_T = (1-x) + \frac{1}{2}(1-x) + x = \frac{1}{2}(3-x)$

$P_A = \dfrac{n_A}{n_T} P$ ∴ $P_{SO_2} = \dfrac{2(1-x)}{3-x}P$, $P_{O_2} = \dfrac{1-x}{3-x}P$, $P_{SO_3} = \dfrac{2x}{3-x}P$

$K_p^2 = \dfrac{\left(\frac{2x}{3-x}\right)^2 P^2}{\left[\frac{2(1-x)}{3-x}\right]^2 \left[\frac{1-x}{3-x}\right] P^3} = \dfrac{(3-x)x^2}{(1-x)^3 P} = (1.876)^2$ ∴ $x = 0.1$

∴ $P_{SO_2} = 0.43$ $P_{SO_3} =$
   $P_{O_2} = 0.242$

# Chap. 12. Reaction Involving Pure <u>Condensed Phases</u> & a <u>Gaseous Phase</u>:

12.1. Intro.

Practical motivation

→ reactions of pure metal to form oxides, sulfides, halides.
→ oxidation at 60λ.
→ T. P. condition for the decomposition of carbonate
→ In such sys., equil^m between ① the gas phase & the indivi condense phases ② bet'n various species in the gas phase.

⟹ temp sensitivity of the sat. vap. press. of pure condensed phases
press. insensitivity of f.E. of species in condensed phase
→ make our life easier.

12.2. Rxn. Equil^m in a sys. containig condensed phases & a g

at T. P. $M_{(s)} + \frac{1}{2}O_2(g) = MO_{(s)}$.
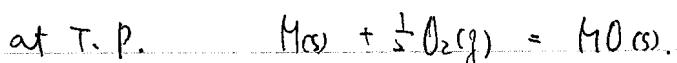
if Oxy. is insoluble to metal. $\left(\dfrac{m_{(s)}}{m_{(s)}}\right)$ $\left(\dfrac{MO_{(s)}}{MO_s}\right)$

For Equil^m chemical potential μ

(12.2) $\overline{G}_M$ (in the gas) = G_M (in the solid). [= in the solid mixture)

(12.3) $\overline{G}_{MO}$ (") = G_{MO} (").
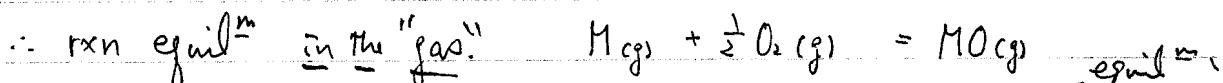
∴ rxn equil^m in the "gas" $M_{(g)} + \frac{1}{2}O_2(g) = MO_{(g)}$ equil.
pressure solid
(12.1) $\Delta G° = G°_{MO(g)} - G°_{M(g)} - \frac{1}{2}G°_{O_2(g)} = -RT \ln \dfrac{P_{MO}}{P_M P_{O_2}^{1/2}}$
uniquely

Since $\boxed{\overline{G}_i = G°_i + RT \ln p_i}$ for each component gas i by temp
in a perfect gas mixture.∴ P_{O_2} →

(12.2) → $G°_{M(g)} + RT \ln p_{M(g)} = G°_{M(s)} + \displaystyle\int_{p=1}^{P=P_{M(g)}} V_{M(s)} \, dP$

(12.4) $dG = -SdT + vdP + \Sigma\mu_i dn_i$

$\overline{G}_M(T.P) - G_M(T, P=1) = \displaystyle\int_{T_i=T}^{12=T} -SdT +$

$\Delta G = \Delta H - T\Delta S.$

(12.5) $G^{\circ}_{MO(g)} + RT \ln P_{MO(g)} = G^{\circ}_{MO(s)} + \int_{P=1}^{P=P_{MO(g)}} V_{MO(s)}\, dP.$

from (12.4) using Fe as an example.

$$G^{\circ}_{Fe(g)} + \boxed{RT \ln P_{Fe(g)}} = G^{\circ}_{Fe(s)} + \int_{P=1}^{P_{(g)}} \boxed{V_{M(s)}}\, dP. \quad ① \quad \underbrace{}_{7.34\,cm^3}$$

$\overbrace{-0.74\,J}$

$\therefore G^{\circ}_{Fe(g)} \gg$

at 1000°C. $P_{Fe(g)} = 6 \times 10^{-10}\, atm.$ $\therefore -224,750\, J.$ at 1000°

$② \int v\, dp \simeq$

(12.4) $\therefore \boxed{G^{\circ}_{M(g)} + RT \ln P_{M(g)} = G^{\circ}_{M(s)}}$

$\therefore$ the standard state of a species occuring as a condensed
can be defined as the pure species at the temp. T.
No need to include $P=1$ atm as a condition.''

Equil^{m} (g+s) Similarly $G^{\circ}_{MO(g)} + RT \ln P_{MO(g)} = G^{\circ}_{MO(s)}.$

Equil^{m} (g+g): (12.1) $G^{\circ}_{MO(g)} - \frac{1}{2} G^{\circ}_{O_2(g)} - G^{\circ}_{M(g)} = -RT \ln \frac{P_{MO}}{P_M P_{O_2}^{1/2}}$

$$= \left(G^{\circ}_{MO(s)} - RT \ln P_{MO(g)} \right) - \frac{1}{2} G^{\circ}_{O_2(g)} - \left(G^{\circ}_{M(s)} - RT \ln P_{M(g)} \right)$$

$$= G^{\circ}_{MO(s)} - \frac{1}{2} G^{\circ}_{O_2(g)} - G^{\circ}_{M(s)} + RT \ln \frac{P_{M(g)}}{P_{MO(g)}} = -RT \ln \frac{P_{MO(s)}}{P_{M(g)}}$$

$$\therefore \boxed{G^{\circ}_{MO(s)} - \frac{1}{2} G^{\circ}_{O_2(g)} - G^{\circ}_{M(s)} = -RT \ln \left(\frac{1}{P_{O_2}^{1/2}} \right)} - K$$

$\neq K$

$\Delta G^{\circ} = -RT \ln K.$

the standard f-E. of the rxn $M_{(s)} + \frac{1}{2} O_2(g) = MO(s).$

For such a sys as $M_{(s)} + \frac{1}{2}O_{2(g)} = MO_{(s)}$ gas + solid.

<u>K</u> can be written only with gas species.

$\Delta G° = f(T)$ only i.e, at a fixed T rxn equil^m $P_{O_2} = P_{O_2(}$

from the phase rule $P = 3$ (MO, M, O_2) $C = (M, O)$

$F = C - P + 2$. $= 2 - 3 + 2 = 1.$ ← Temp.

reduction of / at T $P_{O_2} > P_{O_2(eq. T)}$ → spontaneous oxidation   to reduce P_{O_2}

ores controlled by $P_{O_2} < P_{O_2(eq. T)}$ → reduction to increase P_{O_2}

$\boxed{\begin{array}{l} \text{P265. Example w/ } 4Cu_{(s)} + O_{2(g)} = 2Cu_2O_{(s)} \\ \quad \downarrow \\ \text{267.} \qquad \text{Look at the text.} \end{array}}$

12.3. The Variation of s.f.E. w/ T.

For any chemical rxn $\Delta H_{T_2} = \Delta H_{T_1} + \int_{T_1}^{T_2} \Delta C_p\, dT$, $\Delta S_{T_2} = \Delta S_{T_1} + \int_{T_1}^{T_2} \frac{\Delta C_p}{T}$

$\therefore \Delta G_T° = \Delta H_T° - T\Delta S_T° = \Delta H_{298}° + \int_{298}^{T} \Delta C_p\, dT - T\Delta S_{298}° - T\int_{2}^{T}$

Controls the deviation from linearity bet'n $\Delta G°$ & T.

$\Delta C_p = \Delta a + \Delta b T + \Delta c T^{-2}$

Kirchhoff's Eq. $\left(\dfrac{\partial \Delta H°}{\partial T}\right)_p = \Delta C_p.$ ← known at any temp. T.

$\Delta H_T° = \boxed{\Delta H_0} + \Delta a T + \dfrac{\Delta b T^2}{2} - \dfrac{\Delta c}{T}$

G-Helmholtz $\left(\dfrac{\partial (\Delta G°/T)}{\partial T}\right) = -\dfrac{\Delta H°}{T^2}$

integration const.

integration $\Delta G° = \boxed{I} T + \Delta H_0 - \Delta a T \ln T - \dfrac{\Delta b T^2}{2} - \dfrac{\Delta c}{2T}.$

열!← $\Delta G° = -RT \ln K$. if K is known at any te...

$\boxed{\text{P269.}}$
$\boxed{\underline{131}}$

$$4\,Cu_{(s)} + O_{2(g)} = 2\,Cu_2O_{(s)}$$
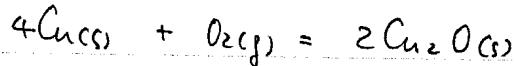
$$\Delta H_{298}^{\circ} = -335,000\ J$$

$$\Delta S_{298}^{\circ} = -152.2\ J/degree.$$

$\bullet\ C_p$ of Cu, Cu_2O, O_2 $\Big\}$ known to Calculate $\underline{\Delta G_T^{\circ}}$

$$\boxed{\Delta G^{\circ} = A + BT\ln T + CT.}$$ $\underline{P_{O_2}}$ (eq. T)

can be changed $\quad = -RT\ln K = -RT\ln \beta_2^{\bullet}$

$$\Delta G^{\circ} = a + bT \quad \text{in a certai temp. range.}$$

vapor pressure eq.

which is similar to $\quad d\ln p = \dfrac{A}{T} + B\ln T + C.$

$\Rightarrow$ Connection. P271 !! w/ $A_{(\ell)} = A_{(v)}$ case.

$$G^{\circ}_{A(\ell)} + \int_1^p V_{A(\ell)}\,dp = G^{\circ}_{A(v)} + RT\ln p_{A(v)}$$

$$\Delta G^{\circ}_{(\ell \to v)} = -RT\ln P_A = -RT\ln K.$$

if $C_{p(\ell)} = C_{p(v)}$ $\quad$ i.e. $\Delta C_p = 0.$ $\longrightarrow$ means $\Delta H \neq f(T).$
$\Delta S \neq f(T)$

$$\ln P_A = -\dfrac{\Delta G^{\circ}}{RT} = -\dfrac{\Delta H^{\circ}}{RT} + \dfrac{\Delta S^{\circ}}{R}.$$

from Clausius-Clapeyron eq.
if $\Delta H \neq f(P,T)$ $\quad \ln P = -\dfrac{\Delta H_{evap}}{RT} + const.$
i.e. $C_{p(v)} = C_p$ (condensed)

if the vapor behaves ideally , at const T . $H_{(v)}$ is indep. of

$$\boxed{\Delta H^{\circ}} = H_v^{\circ} - H_\ell^{\circ} = H_{(v)} - H_{(\ell)} = \boxed{\Delta H_{evap}} \quad \text{indep of } P$$

at const T w/ changing P.

(6.15) $\Delta S = S(P_A, T) - S(1,T) = -\int_1^{P_A} \alpha v\,dp \quad \to S(P_A,T) = S_T^{\circ} - R\ln\dfrac{P_A}{1}$

$\left(\dfrac{\partial S}{\partial p}\right)_T = -\alpha V$ $\qquad = f(T)$

$\therefore \boxed{\Delta S_{(\ell \to v)}} = S_{(v)}^{\circ} - S_{(\ell)}^{\circ} = S_v - S_\ell^{\circ} + R\ln P_A. \boxed{= \Delta S_{evap} + \atop const}$

(7.7) $\dfrac{\Delta S^{\circ}}{R} = const = \dfrac{\Delta S_{evap}}{R} + \ln P_A \qquad \ln P_A = -\dfrac{\Delta H_{evap}}{RT} + \dfrac{\Delta S_{evap}}{R} + 1$

16.4 Ellingham Diagram. $G°-T$ relationships by exp. for oxid. sulfid

ⅰ) (16.9) $\Delta G° = A + BT$ $\left(= IT + \Delta H_0 - \Delta a T \ln T - \frac{\Delta b T^2}{2} - \frac{\Delta c}{2T}\right)$,

the temp.-ind. std. , $\Delta H°$ $-\Delta S°$ identified w/ the neg. of the temp-ind. std. e
enthalpy change (engineering 접근)

ⅱ) Diagram

$\Delta G°$ 0 ┊— $4Ag + O_2(g) = 2Ag_2O$ ┊

462 K

• Oxidati →
이경우 P_{O_2} 가 1atm 보다 커야 $\Delta G° = 0$
즉평형에 도달케되니 P가 reducti →
1atm을 위장한 반응 (Ellingham Dia) 평형 P를 증가시키기 위해 O_2 선성상으로 분식된다)
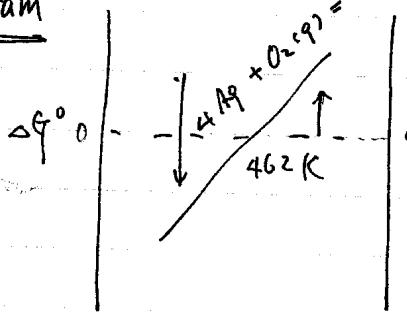
①' $\Delta S_f°$ is a neg. val. (rxn w/ gas di
$-(-k)T = kT$.
    B

①' the line has a pos. slope.

② at 462°K $\Delta G° = -RT \ln k = RT \ln P_{O_2} = 0$
   $(= 2G°_{Ag_2O} - 4G°_{Ag} - G°_{O_2})$

③ $T < 462°K$ $\Delta G° < 0$ Ag_2O more stab

④ $T > ''$ $\Delta G° > 0$ Ag, O_2 ''

⑤ $\Delta G°$ for an oxid. rxn = a measure of the chem. affinity of th
the more neg. the value of $\Delta G°$ at T, the more stable th

ⅲ) about $\Delta S°$.   for the rxn $A + O_2(g) = AO_2(s)$
                                    cancel each other

$$\Delta S° = S°_{AO_2} - S°_{O_2} - S°_A \approx -S°_{O_2}.$$

∴ the std. entropy changes of oxid. involving solid phases are al
the same , parallel each other for "the oxidation" Elling type

ⅳ) about $\Delta H°$ $\Delta H° < 0$ exothermic — most oxidation process.

p275.

$\Delta G°$
ⅰ,ⅱ
— Y + O_2 = YO_2 ⅰ)
   2X + O_2 = 2XO

$\Delta G°_{ⅲ}$
— Y+2XO 2X+O_2
   stable
stable

(ⅰ) $Y + O_2 = YO_2$
(ⅱ) $2X + O_2 = 2XO$.
(ⅰ)-(ⅱ) = $Y + 2XO = 2X + YO_2$.
= (ⅲ)

$\Delta H°_{(ⅲ)}$, $\Delta S°_{(ⅲ)}$ is more neg.

T_E T_E
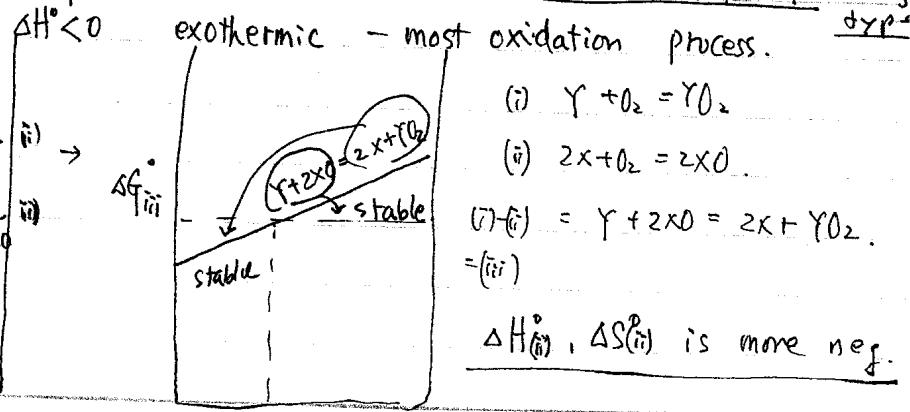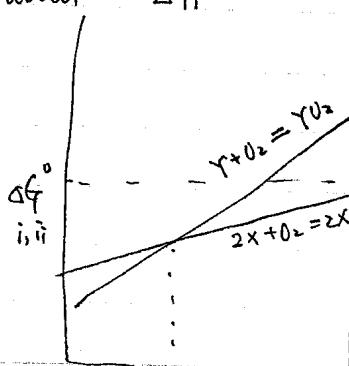
롬 3.10-12 ...there is no one righteous, not even one
...there is no one who understands,
no one who seeks God
All have turned away, they have together become worthless
there is no one who does good, not even one

롬 1:17 The righteous will live by faith.

⑥

For comparison bet'n the stabilities of diff. oxides , the Ellingham diagram.
should be drawn for oxidation rxns involving the consumption o
1 mole of oxygen. $\Delta G° = [$ Energy / 1 mole oxygen $]$.

$$G(P=1, T)$$

→ Richardson. added monographic scale. ⓘ $\Delta G°_T = -RT \ln K$ (10.6)

$$G = G° + RT \ln P.$$ $$(8.10)$$ $\therefore \Delta G = G - G$
$= RT$

for oxidation process $2A + O_2 = 2AO$. $\Delta G°_T = -RT \ln K_f = RT \ln P_{O_2} (T. eq).$

$$\boxed{P \, 277 \, - \, P \, 280}$$!! $B + O_2 = BO_2$ ⓘⓘ   when A. B placed $p = 1$ atm

$R \ln P > 0$ $2A + O_2 = 2AO$ ⓘ   at T_1. Oxidation occurs
to both sys.

$R \ln P < 0$ $T_1 \ T_E \ T_2$ at last. $\underline{BO_2 + A}$

at T_2 " $B + 2AO$
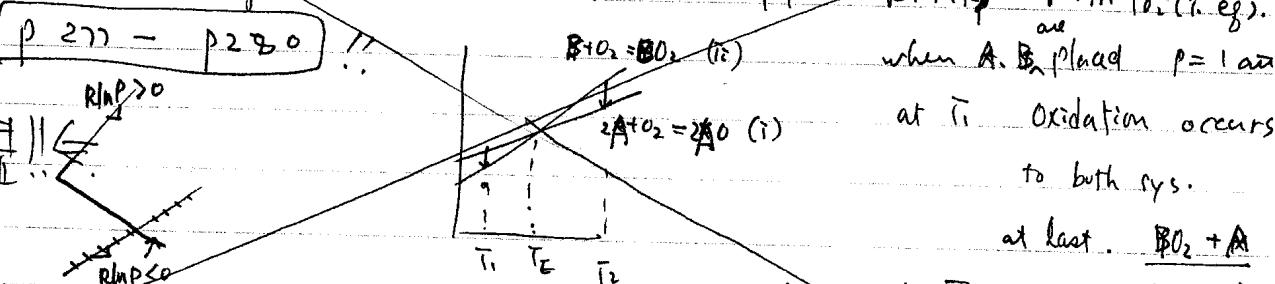
ⓘⓘ $\Delta G°_T$ is seen to be numerically equal to $\Delta G (G - G°)$ of 1 mole at T_E $A + B + AO + B$

the decrease in the $g.f.E$

4.6 of oxygen gas when its pressure is decreased from 1 atm to $P_{O_2 (eq)}$ at equil^m

10.5. The Effect of Phase Transformation.   ⓘⓘⓘ $\Delta G = RT \ln P.$ slope $R \ln P$.

$\Delta H°$ of
high temp phase is high due to the latent heat of the phase chan
$\Delta S°$ of "   "   due to more disordered
→ make → elbow.   a ma

α. $X_{(s)} + O_{2(g)} = XO_{2(s)}$. $\Delta H°$, $\Delta S°$.
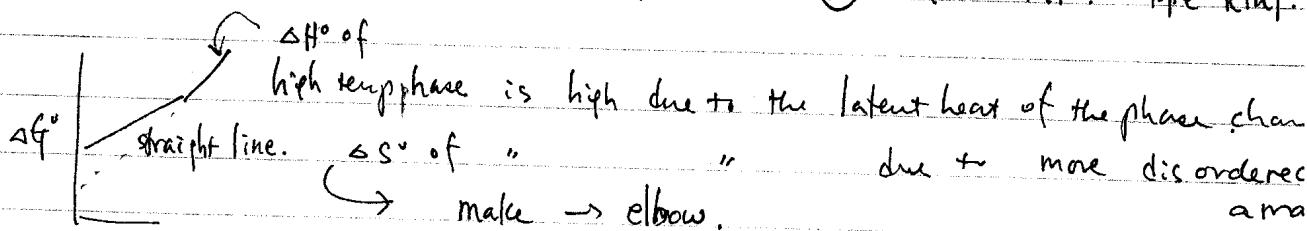
at $T_m . x$. $X_{(s)} = X_{(\ell)}$ $\Delta H°_m$. $\Delta S°_m = \dfrac{\Delta H°_m}{T_m}$

i) $T_{m(XO_2(s))} > T_{m(X)}$ $X_{(\ell)} + O_{2(g)} = XO_{2(s)}$ $\Delta H° - \Delta H°_m$ endo $\therefore$ melt
larger negat

$\Delta S° - \dfrac{\Delta H°_m}{T_m}$ "   th

$$\Delta G° = \Delta H° - T\Delta S°.$$

Since $\Delta H° - \Delta H°_{m-x}$ and $\Delta S° - \Delta S°_{m-x}$ are more negative th $\Delta H°$ & $\Delta S°$, the line in the driagram shows an elbow up
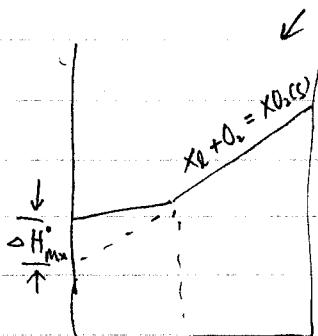
ii) If the melting.p of the oxide Tm_{xO_2} is lower than the m.p. of the metal.

$$X_{(s)} + O_2(g) = XO_2(s)$$
$$\underline{XO_2(s) = XO_2(\ell) \qquad \Delta H°_m \cdot xo}$$

add it up

$$X_{(s)} + O_2 = XO_2(\ell) \qquad \Delta H + \Delta H_m°$$
$$\Delta S° + \Delta S_m°$$
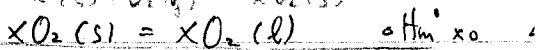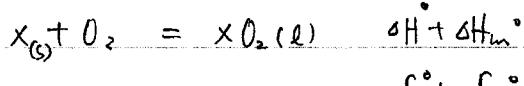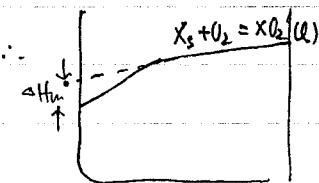
elbow down

if $Tm.x < Tm. xO_2$

if $Tm.x > Tm_{xO_2}$.

Look at p 282 - 286. !!

$$\Delta H_m, FeCl_2 = -T^2 \left[\frac{\partial (\Delta G_m, FeCl_2 / T)}{\partial T} \right] = 59,900 - 12.68 T$$

at 964 K $\Delta H_m = 47.610$.

$$\Delta S_m, FeCl_2 = - \frac{\partial \Delta G_m}{\partial T} = \cdots$$

12.6. | The Oxides of Carbon.
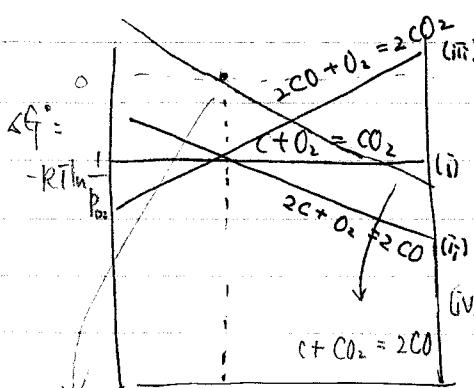
2 moles gas of gas produced from 3 moles of gas
$\Delta S_{iii} = -173$ j
slope = (positive).

1 mole of gas produced from 1 mole of gas $\Delta S_i = 0$

2 moles of   ,, $\Delta S = 17$
slope = (negative

$$\Delta G° = \Delta H° - T\Delta S°$$

$(iv) = (ii) - (i)$ $C_{(gr)} + CO_2(g) = 2CO(g)$

705°c. from (i),(ii) $\Delta G = 2\Delta G_{co} - \Delta G_{co_2}$ (iv) $\Delta G_{(iv)} = 170,000 - 174.5 T$

$$(i) \quad C + O_2 = CO_2 \qquad \Delta G_i^{\circ} = -394,100 - 0.84\,T \quad J \qquad (\text{Horizon}$$

$$(ii) \quad 2C + O_2 = 2CO \qquad \Delta G_{ii}^{\circ} = -223,400 - 175.3\,T \quad J$$

$\boxed{(iii) = 2(i) - (ii)}$ $\quad 2CO + O_2 = 2CO_2 \qquad \Delta G_{iii}^{\circ} = -564,800 + 173.62\,T \quad J$

(*) Consider the equil^M

978 K
ofscaret

$\boxed{(iv) = (ii) - (i)}$ $\quad C + CO_2 = 2CO \qquad \Delta G_{iv}^{\circ} = 170,000 - 174.5\,T$

$\Delta G_{iv}^{\circ} = 0$ at $T = 978\,K$ where CO & CO_2, both at 1 atm. (s. st

∴ rxn (iv) $\Delta G_{978}^{\circ} = 0 = -RT \ln\left(\dfrac{P_{CO}^2}{P_{CO_2}}\right)$ ∴ total pressure = 2 atm

$\longrightarrow 1$

(A) If total pressure $= 1$, $P_{CO} = P_{CO_2} = 0.5$ then $T_{eq} = ?$ eq $\Rightarrow K = 1$.

Equil^M (T_{978}) $\Rightarrow K = 1 = \dfrac{P_{CO}^2}{P_{CO_2}}$ and $P_{CO} + P_{CO_2} (= 0.5 + 0.5) = 1$ atm.

① P total ↓, P_{CO} ↑ to increase P then $P_{CO} > P_{CO_2}$ $\quad C + CO_{2(g)} = 2CO$
by Le Chatelier's prin. $\longrightarrow$

② $\Delta H^{\circ} > 0$ endo ($+ 170\,KJ$) ∴ As T↓ rxn goes to produce
heat $\quad C + CO_{2(g)} = 2CO$ (열재흡) $\longleftarrow$

③ ∴ if required to decrease the P of the system from 2 to 1
maintaining $P_{CO} = P_{CO_2}$, then the T must be decreased

Ⓑ * How to calculate T_{eq} to make $P_{CO(eq)} = P_{CO_2(eq)} = 0.5$

i) $C + O_2 = CO_2$ (1 atm)

$\boxed{\text{v)}}$ $CO_2 (T. P=1) = CO_2 (T. P=0.5)$ $\qquad \Delta G_v = RT \ln 0.5$
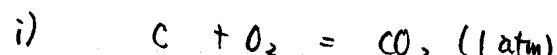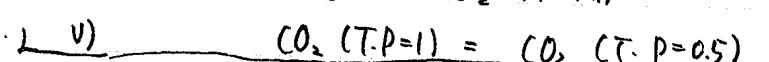
vi) $C + O_2 (P=1) = CO_2 (P=0.5)$ $\qquad \Delta G_{vi} = -394,100 - 0.84\,T + RT \ln($

$\boxed{(vi) = (i) + (v)}$ $(= \Delta G_i^{\circ} + RT \ln 0.5)$

$\Delta G = -s\,dT + \int v\,d$
$= RT \ln$
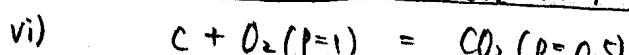
F.12.14
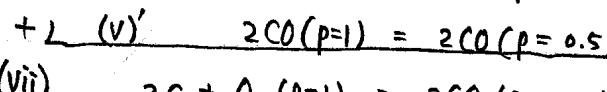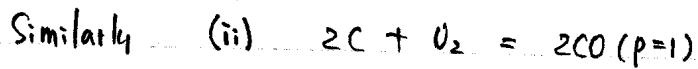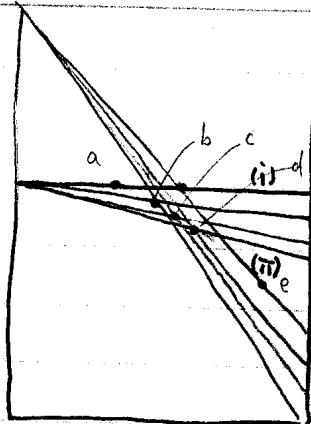
$C + O_2 = CO_2 (1 atm)$
$= CO_2 (0.75 atm)$
$= CO_2 (0.5 atm)$
$= CO_2 (0.25)$

$2C + O_2 = 2CO$ (1)
$= 2CO (0.75)$
$= 2CO (0.5)$
$= 2CO (0.25)$

temp.

$\therefore$ $CO_2 (p=0.5)$, $CO(p=0.5)$ are in equil^m w/ solid C at that temp
where $\Delta G_{viii} = 0$ (point C)

* line a-b-c-d-e is the locus of $P_{total} = 1$ atm. with varying CO, CO_2

p. 12.15

% CO

600   1000   1400K
Temp.

application

Similarly   (ii) $2C + O_2 = 2CO (p=1)$
+ 2 (v)' $2CO(p=1) = 2CO(p=0.5$
(vii) $2C + O_2(p=1) = 2CO (p=0.5)$

$\Delta G_{vii} = -223,400 - 175.3 + 2RT\ln$
$= \Delta G_{ii}^\circ + 2RT \ln 0.5$

$(viii) = -(vi) + (vii)$ gives

(viii) $C_{(gr)} + CO_2 (p=0.5) = 2CO(p=0.5)$

$\Delta G_{(viii)} = \boxed{\Delta G_{(iv)}^\circ} + RT\ln 0.5$ $(-RT$

$\Delta G_{ii}^\circ - \Delta G_i^\circ$
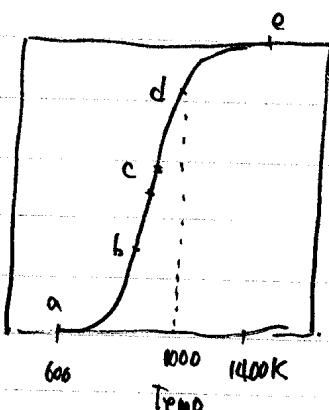
$T < 600K$ the equil^m gas is CO_2 at 1 atm.
$T > 1400K$ " CO at 1 atm.

reduction

ⓒ At any temp. T   the $CO-CO_2$ mixture in equil^m w/ C exerts an
$P_{O_2 (eq)}$ via $2CO + O_2 = 2CO_2$ (iii)

$\Delta G_{iii}^\circ = -RT \ln \dfrac{P_{CO_2}^2}{P_{CO}^2 P_{O_2}} = 2RT \ln \left(\dfrac{P_{CO}}{P_{CO_2}}\right)_{eq.w/c} + RT \ln (P_{O_2 (eq)})$

$\therefore$ for rxn $M + O_2 = MO_2$.   in order to reduce MO_2, P_{O_2} to use
for reduction process should be lower than $P_{O_2 (eq. T)}$ when C was
used as a reducing agent $\Rightarrow P_{O_2} < P_{O_2 (eq. T)}$

The Equil^M $2CO + O_2 = 2CO_2$

F. 12.16
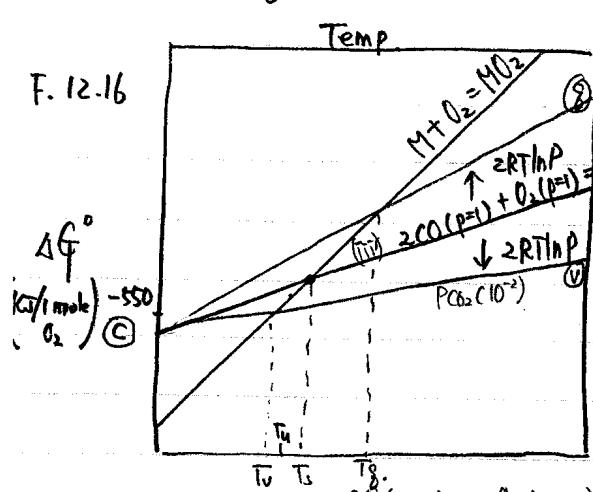
For the rxn above in Ellingham diagr
line CS → O_2 (p=1), CO_2 (p=1), CO (p=1)
$\Delta G^\circ(T)$ for the rxn to produce CO_2 (1atm) from CO (1atm)

∴ the effect of producing CO_2 at any pres
other than 1 atm (from CO, O_2 1atm e
is the rotation of the E. diagram line C
about the pt. c.   c.w if $P_{CO_2} < 1$ atm
                        c.c.w if $P_{CO_2} > 1$ atm

$2CO(p=1) + O_2(p=1) = 2CO_2(p=1)$ $\Delta G^\circ_{(iii)}$

$+ 2$ $2CO_2(p=1) = 2CO_2(p=p)$ $\Delta G = RT \ln p^2$ $\{dG = \int -s\,dT + \int_1^p v\,dp$

$2CO(p=1) + O_2(p=1) = 2CO_2(p=p)$ ∴ $\Delta G = G - G^\circ = \int_1^p \frac{RT\,dp}{P}$
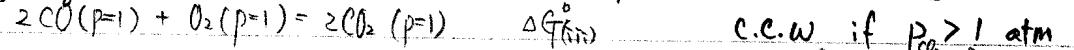
$\Delta G = \Delta G^\circ_{(iii)} + 2RT \ln P$ if $P > 1$ $\ln P > 0$ c.c.w

(ix) T_s, the temp. at which the s.f.E. for $MO_2 + 2CO = M + 2CO_2$ is zero

ΔG°_{ix} at $T_s = 0 = -RT \left(\frac{P_{CO_2}}{P_{CO}}\right)^2$ ∴ $P_{CO_2} = P_{CO}$ $(P_{CO_2}/P_{CO}$

at $T (= T_g) > T_s$ MO_2 unstable   reducing
at $T (= T_u) < T_s$ MO_2 stable   oxidizing

⇒ if want to reduce MO_2 at $T < T_s$? then P_{CO_2}/P_{CO_2} ↕ (or P_{CO}/P_{CO_2} ↕

(x) ex.   at T_u ($P_{CO}/P_{CO_2} = 10$) $MO_2 + 2CO(1atm) = M + 2CO_2$ (a.1 atm)

ΔG_x at T_u $= \Delta G^\circ_{ix} + 2RT \ln 0.1$

$= -RT \ln \left(\frac{P_{CO_2}}{P_{CO}}\right)^2_{eg} + 2RT \ln 0.1$

∴ $\Delta G_x = 0 =$ "   "

∴ $P_{CO}/P_{CO_2} = 10.0$

⇒   Conclusion. by decreasing the temp. from T_s to T_u, the CO_2/CO ratio
should be down from 1 to 0.1 to maintain the rxn.

⇒   Use of

⇒ Similarly at T_v the equil^m CO/CO_2 ratio = 100

at T_g ″ = 0.01

∴ a CO/CO_2 nomographic scale can be added to the E. diagram for any rxn $MO_2 + 2CO = M + 2CO_2$.

F. 12.13

Fig 12.15
%CO

temp.
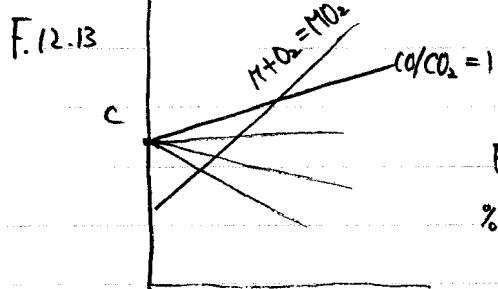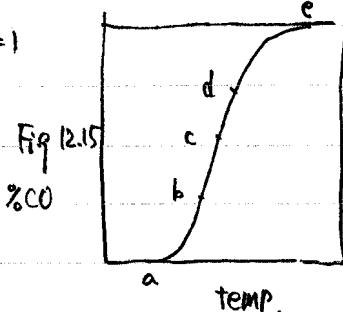
Fig. 12.15 can be read off from F. 12.13

a b c d e 를 구하는법 ① (i) 과 (ii)를 rot (P에 맞게) 하여 구하는법.

② nomograph 상

Similarly the H_2/H_2O nomographic scale. ($2H_2 + O_2 = 2H_2O$) for the rxn

$MO_2 + 2H_2 = M + 2H_2O$