3.020 Lecture 31

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1 Reactions between gases and condensed phases

not just for ideal gases

- in general $a\,\mathrm{A} + b\,\mathrm{B} \longleftrightarrow c\,\mathrm{C} + d\,\mathrm{D}$

$$\begin{aligned}
dG^{'} &= \sum_i \mu_i dn_i = \sum_i \mu_i \nu_i d\xi, \quad \frac{dn_i}{\nu_i} = d\xi \\
\mu_i &= \mu_i^o + RT \ln a_i \\
dG^{'} &= (\sum_i \mu_i^o \nu_i + RT \sum_i \ln a_i^{\nu_i}) d\xi \\
&= (\Delta G^o + RT \ln (\prod_i a_i^{\nu_i})) d\xi \\
&\Longrightarrow \quad \textbf{At equilibrium,} \quad \prod_i a_i^{\nu_i} = e^{-\Delta G^o/RT}
\end{aligned}$$

- Equilibrium constant for metal oxidation $\mathrm{zM} + \mathrm{O_2} \longleftrightarrow \mathrm{M}_z\,\mathrm{O_2}$

$$K = \frac{a_{MzO_2}}{a_M^z a_{O_2}}$$

  - Treat $\mathrm{O_2}$ as an ideal gas, $a_{O_2} = P_{O_2}/atm$
  - Assume condensed phases are pure, $a_M = a_{M_zO_2} = 1$

$$K = (P_{O_2}/atm)^{-1} = e^{-\Delta G^o/RT}$$

- Evaluating $\Delta G^o = \Delta H^o - T\Delta S^o$ for metal oxidation
  1. Enthalpy $\Delta H^o = \Delta H^o_{298} + \int_{298}^{T} dT^{'} \Delta C_P$
     - For most metal oxides ΔH^o_{298} is large
     - Due to exothermic nature of metal-oxygen band formation $\longrightarrow$ Neglect temp. dependence, simplify as

$$\Delta H^o \approx \Delta H^o_{298}$$

  2. Entropy $\Delta S^o = \Delta S^o_{298} + \int_{298}^{T} dT^{'} \frac{\Delta C_P}{T^{'}}$

- Entropy is dominated by condensation of O_2 out of gas phase $\longrightarrow$ Neglect temp.dependence, simplify as

$$\Delta S^o = \Delta S^o_{298}$$

- Solve for P_{O_2}

$$P_{O_2}/atm = e^{\Delta H^o/RT} e^{-\Delta S^o/R}$$

  Oxygen pressure at which a metal and its oxide coexist at equilibrium

  - Higher P_{O_2}: Metal spontaneously oxidized
  - Lower P_{O_2}: Oxide spontaneously reduced

e.g. $Ti + O_2 \longleftrightarrow TiO_2$ at 298 K, $P_{O_2} \approx 10^{-130}$ atm

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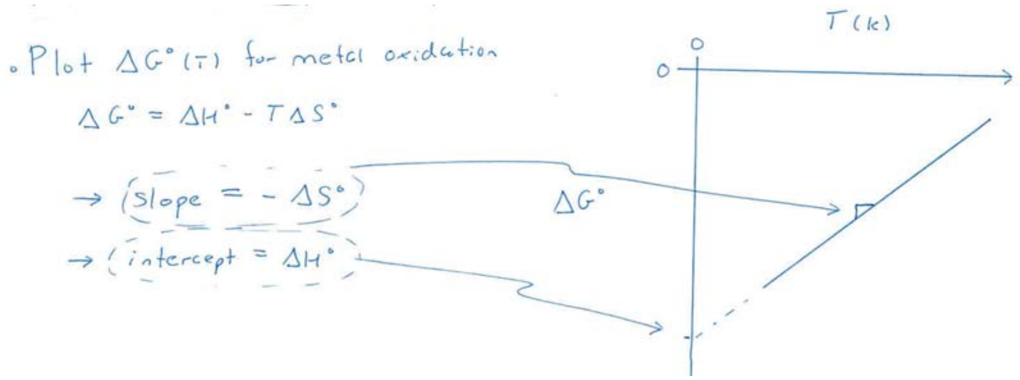
2 Richardson-Ellingham diagrams



- Plot $\Delta G^\circ(T)$ for metal oxidation

  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

  → (slope $= -\Delta S^\circ$)

  → (intercept $= \Delta H^\circ$)

- The P_{O_2} scale

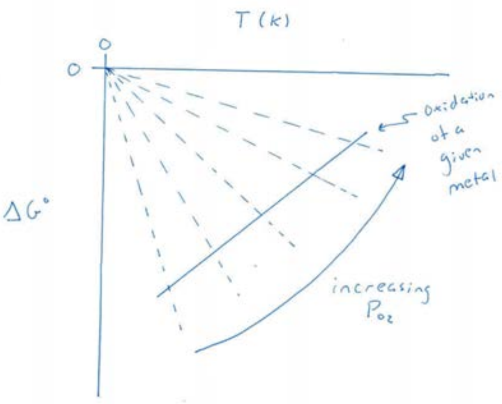
$$K_P = (P_{O_2}/atm)^{-1} = e^{-\Delta G^o/RT}$$

$$\downarrow$$

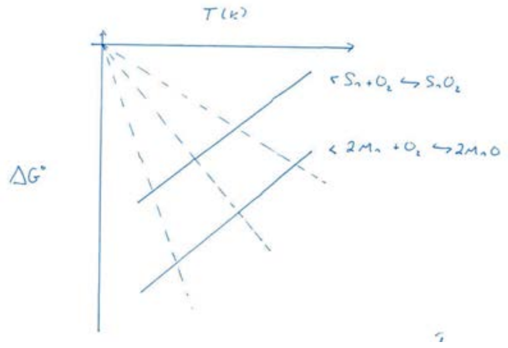
$$\underbrace{\Delta G^o = RT\ln(P_{O_2}/atm)}$$

line on $\Delta G^o(T)$ with

  - slope $R\ln P_{O_2}/atm$
  - zero intercept



- Why is this useful ? Materials processing
  e.g. consider two metals, Sn and Mn



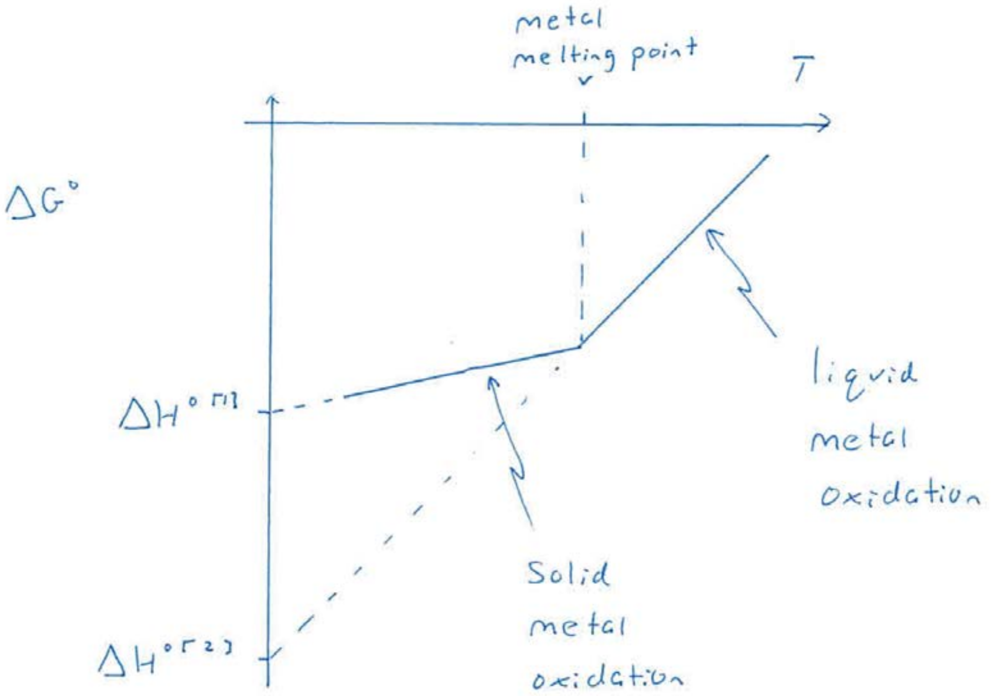
- At given pressure, P_{O_2} for Mn oxidation rxn. is lower than that for Sn oxidation
- Mn metal will reduce Sn oxide
- Mn has greater affinity for oxygen than does Sn
- ΔH^o is more negative for Mn oxidation than for Sn oxidation
- Mn metal "pull" oxygen out of Sn oxide

All expressing the same thing, about metal-oxygen bonds

3 Effect of phase transitions

- Melting of the metal or its oxide
- Causes discrete jumps in ΔH^o and ΔS^o e.g.
  (1) $\mathrm{M}^{\alpha} + \mathrm{O}_2 \longleftrightarrow \mathrm{M\,O_2}^{\mathrm{S}}$, $\Delta S^{o[1]}$
  Now raise temp. s.t. metal melts consider case when metal has lower M.P. than oxide
  (2) $\mathrm{M}^{\mathrm{L}} + \mathrm{O}_2 \longleftrightarrow \mathrm{MO_2}^{\mathrm{S}}$, $\Delta S^{o[2]}$
  Liquid has higher entropy than solid

$$\Delta S^{o[2]} < \Delta S^{o[1]}$$


metal melting point
T
ΔG°
ΔH°[1]
ΔH°[2]
liquid metal oxidation
Solid metal oxidation

3.020 Thermodynamics of Materials
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