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On Gibbs free energy

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etc.

饱和蒸气压

- 饱和蒸气压概念
  - 将一杯纯溶液置于密闭的钟罩内，一定时间后液面将有所下降，直到罩内气体压力达到一定数值为止。此时的气体压力称为该液体的饱和蒸气压，简称蒸气压。分子运动学，蒸发与凝聚的速度相等时，气液两相达到动态平衡。
- 饱和蒸气压的应用
  - 凝聚态某组元的化学势
  - 化学反应气相的化学势
- 例子

	液相	气相
A	G(A)	P1
B	G(B)	P2

平衡条件

$$G(A,liquid)=G(gas,P1)$$
$$G(B,liquid)=G(gas,P2)$$

$$\Delta G(A\rightarrow B,liquid)=\Delta G(gas,P1\rightarrow P2)$$

$$\Delta G(gas,P1\rightarrow P2)=\int_{P1}^{P2}dG$$

5.1 THERMODYNAMIC ACTIVITY (2)

$$\alpha_i \equiv \frac{f_i}{f_i^\circ}$$

No Units
Reference state: temperature, pressure and physical form
Standard state: pressure and physical form

Gas: pure gas at one atmosphere
Condensed mater: pure liquid or solid under one atmosphere

$$\int_{\underline{G}^\circ}^{\overline{G}} dG_i = \overline{G}_i - \underline{G}_i^\circ = RT \ln \frac{f_i}{f_i^\circ} = RT \ln \alpha_i$$

$$\int_{\underline{G}^\circ}^{\overline{G}} dG_i = \overline{G}_i - \underline{G}_i^\circ = RT \ln \frac{P_i}{P_i^\circ} = RT \ln \alpha_i$$ Ideal gas

The fugacity of a condensed phase is equal to the fugacity of the vapor in equilibrium with it.

The value of thermodynamic activity changes not only with pressure but also with composition.

5.2 CHEMICAL EQUILIBRIUM

$$bB + cC = dD + eE$$

Expression for a chemical reaction

$$\delta W_{rev} = \Delta G = d\overline{G}_D + e\overline{G}_E - b\overline{G}_B - c\overline{G}_C$$

$$\overline{G}_B = \overline{G}_B^{\circ} + RT\ln\alpha_B$$

$$\Delta G = d(G_D^{\circ} + RT\ln\alpha_D) + e(G_E^{\circ} + RT\ln\alpha_E) - b(G_B^{\circ} + RT\ln\alpha_B) - c(G_C^{\circ} + RT\ln\alpha_C)$$

$$\Delta G = 0$$

$$\Delta G = \Delta G^{\circ} + RT\ln J_{\alpha}$$

$$\Delta G^{\circ} = dG_D^{\circ} + eG_E^{\circ} - bG_B^{\circ} - cG_C^{\circ}$$

Equilibrium constant

$$J_{\alpha} = \frac{\alpha_D^d \alpha_E^e}{\alpha_B^b \alpha_C^c}$$

$$\Delta G^{\circ} = -RT\ln J_{\alpha(equilibrium)} = -RT\ln K_{\alpha}$$

5.6 ELLINGHAM DIAGRAMS (4)

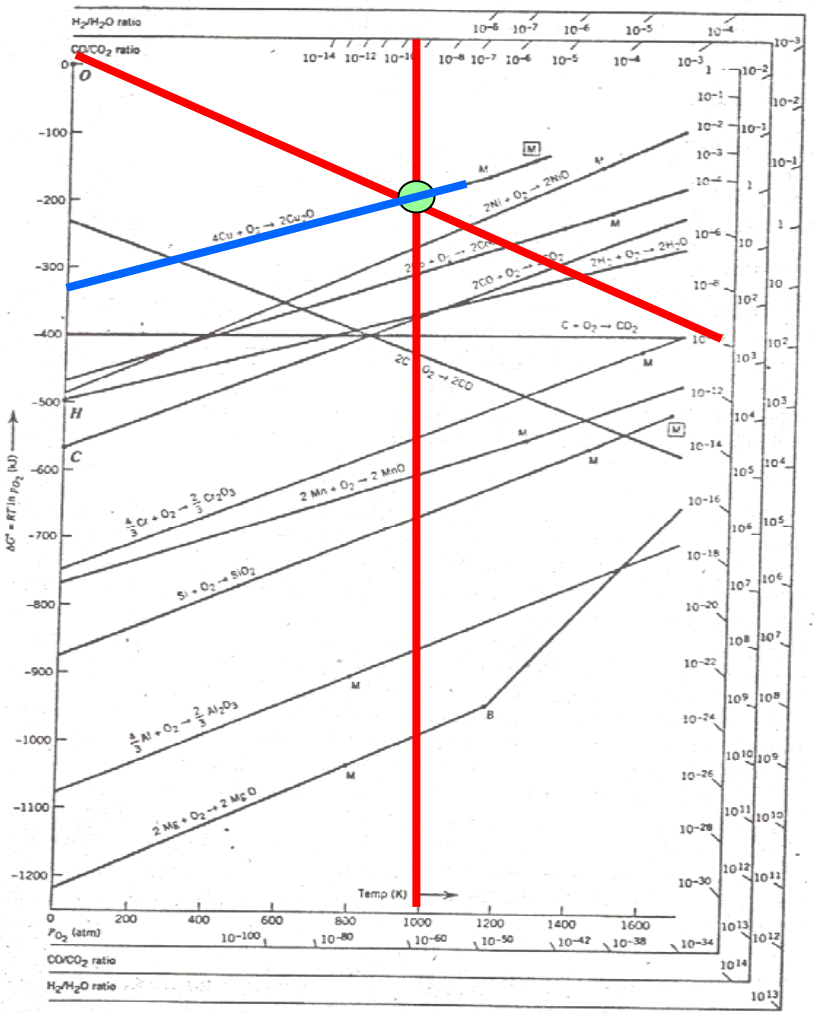

Figure 5.7 Ellingham diagram for some oxides.

1. 直线位置越低，元素与氧化合的能力越大，相应的氧化物越稳定；
2. 位置在下的金属或元素可以把较上面的金属从氧化物中 还原出来；
3. 炼铁过程，铁以下进入炉渣，铁以上进入铁液，决定何时加入配料。

局限

平衡的热力学讨论

凝聚相都是纯物质