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ALSO PRACTICE NOW

Ellingham Diagrams

- Ceramics are processed and often used at high temperature
- Therefore they are environmentally sensitive.
- Ellingham diagrams & equivalent approaches provide us quantitative information based upon THERMODYNAMIC EQUILIBRIA.

For example

* (i) $Ni + Cu_2O \rightleftharpoons NiO + 2Cu$.

will the reaction go to the right or two the left. Why does it depend on the p_{O_2} in the environment.

* (ii) $4Cu + O_2 = 2Cu_2O$

How does the direction of the reaction depend on p_{O_2}.

* (iii) How will the reaction in (ii) depend on the atmosphere ~~well~~ which is a ratio of p_{CO}/p_{CO_2}.

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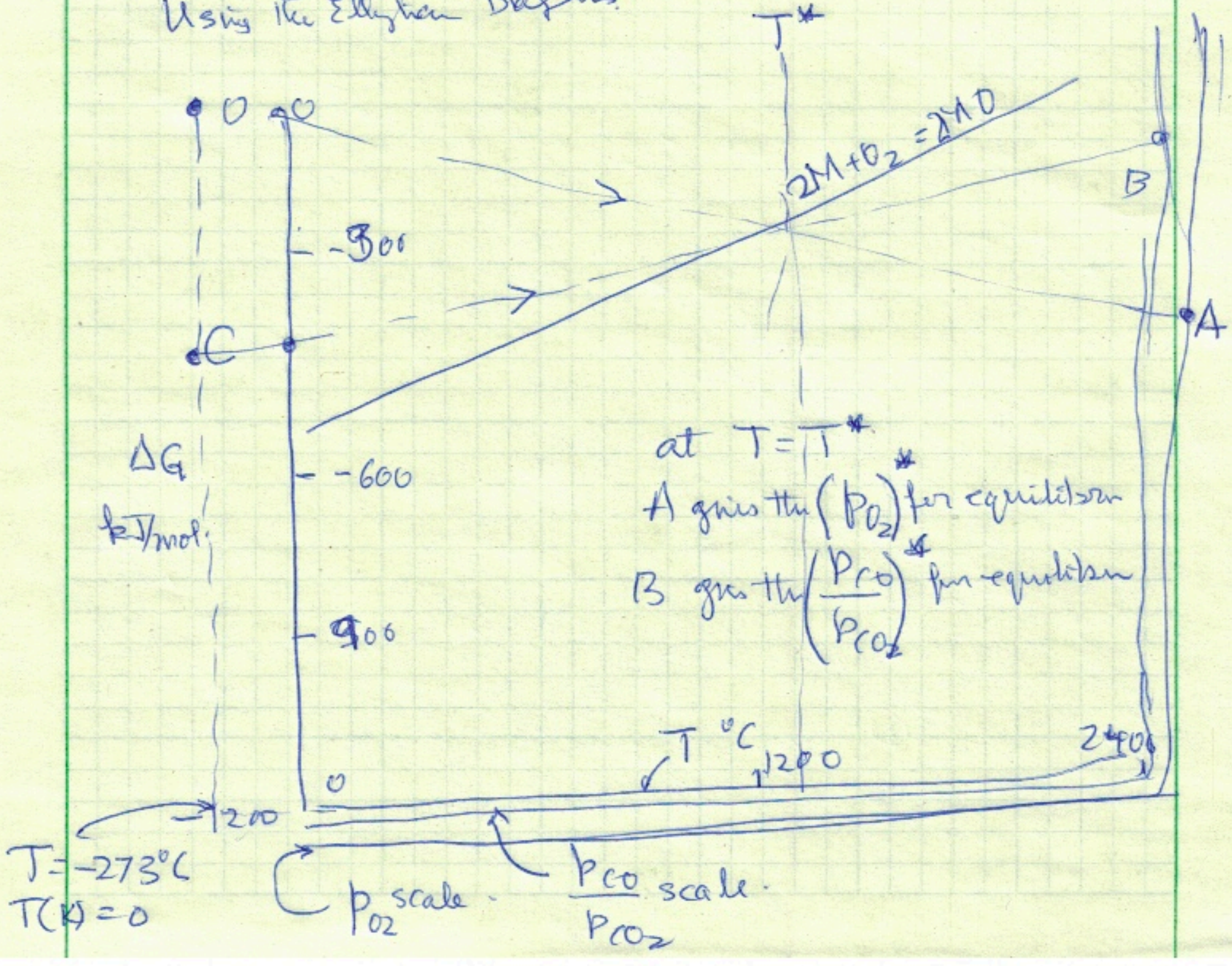
* (iv) $2SiC + 3O_2 = 2SiO_2 + 2CO$ — ①

$SiC + 2O_2 = SiO_2 + CO_2$ — ②

Q. • which reaction is more likely at higher temperature?

• At a given T calculate the equation that gives the P_{O_2} activities which attain equilibrium in ① & in ②.

Using the Ellingham Diagram.



at $T = T^*$

A gives the $(P_{O_2})^*$ for equilibrium

B gives the $\left(\frac{P_{CO}}{P_{CO_2}}\right)^*$ for equilibrium

- MO will reduce to M & O_2 if

$$p_{O_2} < (p_{O_2})^* \quad \text{③}$$

- MO will reduce to M & O_2 if

$$\left(\frac{p_{CO}}{p_{CO_2}}\right) < \left(\frac{p_{CO}}{p_{CO_2}}\right)^*$$

Questions

(V) Show how the Ellingham diagram is drawn for different values of p_{O_2} and T for the reaction

$$\underset{(crystal)}{2M} + \underset{(gas)}{O_2} = \underset{(crystal)}{2MO} \quad \text{④}$$

(Vi) Show how the diagram is drawn for different values of $\frac{p_{CO}}{p_{O_2}}$ for

$$2M + O_2 = 2MO$$

(Vii) Why do we need to specify if the material is a crystal, glass, liquid or gas?

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BACKGROUND

Chemical potential

$$\mu_{M}(T,p) = \mu^{\circ}_{m}(T) + RT\ln a_c$$

M ↑ species

a_c ↑ depends on pressure & purity.

$$\mu_{O_2}(T,p) = \mu^{\circ}_{O_2}(T) + RT\ln a_{O_2}$$

$a_{O_2} = p_{O_2}$ (atm press).

Activity is defined relative to a standard state. For example the standard state of

$p_{O_2} = 1$ atm. $\quad a_{O_2} = \dfrac{p_{O_2}}{p_{O_2}(1\,\text{atm})} = p_{O_2}$ expr in atm.

Reaction thermodynamics

$$2M + O_2 = 2MO.$$

Equilibrium →

$$2\mu_{M} + \mu_{O_2} = 2\mu_{MO}. \quad (\text{at } T, \& \ p_{O_2}).$$

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$$2\mu_{MO} = 2\left[\mu^0_{MO} + R\ln a_{MO}\right]$$

etc.

$$\therefore\ 2\mu_{MO} - 2\mu_{M} - \mu_{O_2}$$

$$= \underbrace{\left[2\mu^0_{MO} - 2\mu^0_{M} - \mu^0_{O_2}\right]}_{\text{given by Janaf tables as a function of T. at 1 atm pressure.}} + RT\ln\frac{a^2_{MO}}{a^2_{M}\,a_{pO_2}} = 0$$

for equilibrium

$$\Delta G_{JANAF} = RT\ln p_{O_2} + RT\ln\frac{a_M^2}{a_{MO}^2}$$

$a_M = a_{MO} \approx 1$ since it does not change with pressure.

$$\therefore\ \Delta G_{JANAF} = RT\ln p_{O_2} \quad \text{—} \quad ⊗ \quad ⑤$$

* Q. why does ΔG_{JANAF} have a positive slope with temperature

* Q. why does $RT\ln p_{O_2}$ have a negative slope wrt temp.

~~35~~

~~0.03 Ωm^2 × 40Ω = $\frac{10V}{0.25}$~~ ~~1.2 Ωcm^2~~

~~50 mA/mm^2~~ ~~250mA~~

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Equilibrium with $\frac{p_{CO}}{p_{CO_2}}$ ratio.

Consider the Reaction

$$2CO + O_2 = 2CO_2 . \quad -⑥$$

$$\Delta G^{CO_2}_{JANAF} = \cancel{G_{CO_2} - \frac{1}{2}G_{O_2} - \frac{1}{2}G_{CO}} \rightarrow \frac{1}{2}\{2G_{CO_2} - G_{O_2} - 2G_{CO}\}.$$

Equilibrium condition

$$2\,\Delta G^{CO_2}_{JANAF} + RT \ln \frac{p_{CO_2}^2}{p_{O_2}\,p_{CO}^2} = 0. \quad -⑦$$

write equation ⑦ as.

$$2\,\Delta G^{CO_2}_{JANAF} - 2RT \ln \frac{p_{CO}}{p_{CO_2}} = RT \ln p_{O_2} \quad -⑧$$

* Q: Use equations (8) & ⑤ to explain how the Ellingham Diagram is used to calculate the equilibrium value of $\frac{p_{CO}}{p_{CO_2}}$ at a given temperature as explained in the text