3.020 Lecture 32

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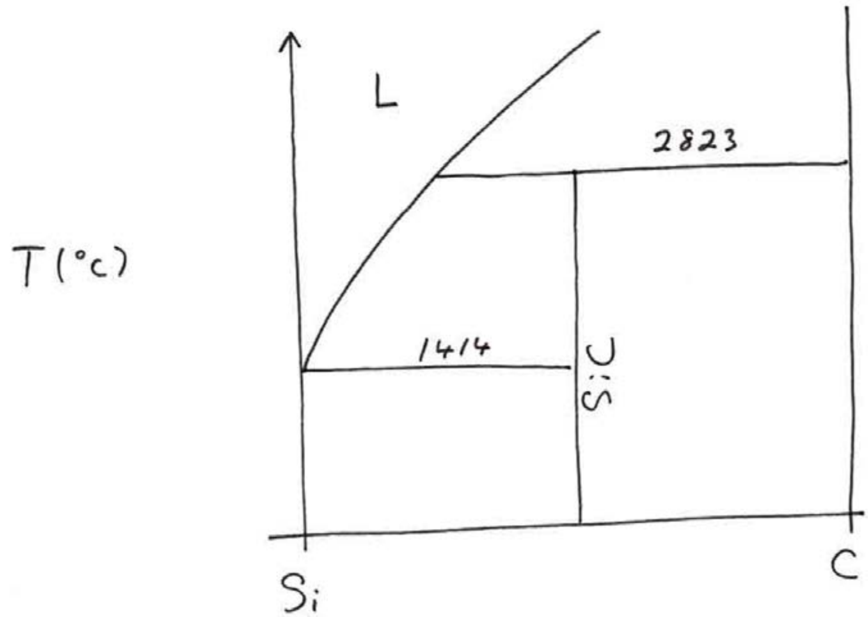
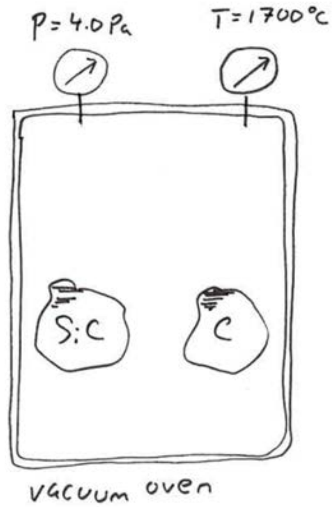
1 Reacting systems with condensed and gaseous phases

Example : Formation of SiC



2 Problem statement

- Place pieces of SiC and C into a vacuum oven
- Pull vacuum (to $P \approx 0\ Pa$), seal, and then heat to 1700 ^oC



You observe:

1. SiC and C are both still present
2. Pressure $P = 4.0\ Pa$

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3 Reference data

- Saturation vapor pressures at 1700 ^oC are

$$P_{Si}^{SAT}(1700\ ^oC) = 4.4Pa$$
$$P_C^{SAT}(1700\ ^oC) \approx P_{SiC}^{SAT}(1700\ ^oC) \approx 0\ Pa$$

Question: What is the Gibbs free energy of formation of SiC at 1700 ^oC ?

$$\mathrm{Si}^{\alpha} + \mathrm{C}^{g} \xleftrightarrow{\Delta_f\,\mathrm{G}} \mathrm{SiC}$$

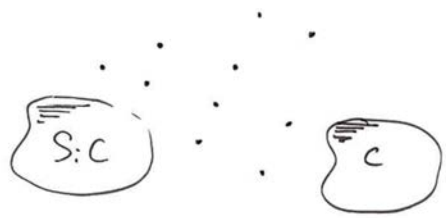
$$\Delta_f G_{SiC} = G_{SiC} - G_{Si}^o - G_c^o$$

For 1 mole of SiC

$$G' = \sum_i n_i^{SiC}\mu_i^{SiC} = \mu_i^{SiC} + \mu_c^{SiC}$$
$$(n_{Si}^{SiC} = n_C^{SiC} = 1)$$
$$\Delta_f G_{SiC} = \mu_{Si}^{SiC} + \mu_C^{SiC} - \mu_{Si}^o - \mu_C^o$$
$$= \underbrace{(\mu_{Si}^{SiC} - \mu_{Si}^o)}_{II} + \underbrace{(\mu_C^{SiC} - \mu_C^o)}_{I}$$

(I) How does the chemical potential of C differ from its pure, reference state ?
It doesn't ! Pure C is in equilibrium with SiC

$$\mu_i^{SiC} = \mu_C^g = \mu_C^o$$



C atoms exchanging freely between SiC and C^g via vapor phase
⇓
chemical equilibrium

(II) How does the chemical potential Si differ from its pure, reference state?

- If solid Si were present in the system, the partial pressure P_{Si} would be equal to its saturation value P_{Si}^{SAT}
- Therefore $\mu_{Si} - \mu_{Si}^o = RT \ln (P_{Si}/P_{Si}^{SAT})$, recognizing that Si in SiC is in equilibrium with Si in vapor phase.

- What is P_{Si} ?
  - Total pressure = 4.0 Pa
  - C and SiC are saturated, but their saturation vapor pressure are negligible

  $P_{Si} \approx P = 4.0\ Pa,$ **vapor is essentially pure Si**

$$\mu_{Si} - \mu_{Si}^o = RT \ln (\frac{4.0}{4.4}) = -1,563\ J/mol$$

Therefore,

$$\Delta_f G_{SiC} = (\mu_{Si} - \mu_{Si}^o) - \underbrace{(\mu_C - \mu_C^o)}_{0}$$
$$= RG \ln \frac{4.0}{4.4}$$
$$= -1,563\ J/mol$$

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4 Key to solving such problems

Ask "Who is in equilibrium with whom??"