

CHEM-E6100 FUNDAMENTALS OF CHEMICAL THERMODYNAMICS

EXAMINATION 17.12.2021, 09:00-13:00

Return the answers in the return box in MyCourses latest at 13:00. Remember to send the uploaded file. It is not possible to return after that time. Answers can be written directly in this paper or in a separate document. Scanned documents or pictures are accepted if the quality is high enough to be easily read. All relevant calculation steps should be included in the responses. An equation sheet from previous exams is provided at the end of the document. All questions give a maximum 5 points each, maximum score is 30 points.

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REMEMBER TO ANSWER THE WEBROPOL COURSE SURVEY BEFORE 31.12.2021!

Gas constant $R = 8.314 \text{ J / (mol K)}$

Questions

1. Molybdomancy (“Tinavalanta” in Finnish) is a tradition in Finland during the New Year’s festivities, where molten tin or lead (or an alloy of these metals) is poured into water, and the shape of the frozen metal is interpreted as omens for the upcoming year. Assume a stainless steel pot weighing 0.5 kg filled with 5 kg of H_2O (~5 liter water) at a temperature of $20 \text{ }^\circ\text{C}$.

How much molten lead heated to an initial temperature of $400 \text{ }^\circ\text{C}$ needs to be added to the waterfilled pot for it to reach $30 \text{ }^\circ\text{C}$?

Assume that heat losses to the surroundings (including air) are negligible, that formation of water vapor is negligible, as well as that no chemical reactions between the lead, steel and H_2O occur. (Nowadays, lead is actually forbidden to use for this practice.)

We know the following properties:

Specific heats:

| | specific heat (J / (kg K)) |
|--------------------------------|---------------------------------|
| $\text{H}_2\text{O}(\text{l})$ | 4182.393 |
| $\text{Pb}(\text{s})$ | $117 + 0.0443 * T / \text{K}$ |
| $\text{Pb}(\text{l})$ | $156.5 - 0.1429 * T / \text{K}$ |
| Steel | 500 |

Enthalpy of melting of Pb 23021.24 J/kg

Melting point of Pb $327.5 \text{ }^\circ\text{C}$

2. What is the entropy change when pure silver is heated from 298.15 K to 1300 K?

We know:

$$c_p(\text{Ag, solid}) = 21.30 + 8.54 \times 10^{-3} \times T + 1.5 \times 10^5 / T^2 \text{ (J/(molK))}$$

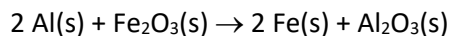
$$c_p(\text{Ag, liquid}) = 33.47 \text{ (J/(molK))}$$

$$\Delta H (\text{melting}) = 11.3 \text{ kJ/mol}$$

$$T(\text{melting}) = 1234 \text{ K}$$

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3. Aluminothermic reduction is a pyrometallurgical method to reduce metal oxides by reacting with metallic aluminium. In the reaction, the products are the metal and Al_2O_3 . The Aluminum-metal oxides mixtures are also called thermite, and are known for their highly exothermic reactions.

Calculate the final temperature of the reacted product mixture in aluminothermic reduction, assuming a starting composition of 1 g Al + 15 g Fe_2O_3 at an initial temperature of 25 °C. The only reaction occurring after ignition is the following:



and assume that the specific reaction equilibrium goes completely to the right in the reaction. Assume that there are no heat losses to the surroundings. Standard enthalpy of the phases are as follows:

$$\text{Al:} \quad H(T)/[\text{J/mol}] = -9281.3 + 31.13 T / \text{K}$$

$$\text{Al}_2\text{O}_3: \quad H(T)/[\text{J/mol}] = -1\,695\,330.6 + 129.02 T / \text{K}$$

$$\text{Fe:} \quad H(T)/[\text{J/mol}] = -11\,820 + 39.646 T / \text{K}$$

$$\text{Fe}_2\text{O}_3: \quad H(T)/[\text{J/mol}] = -867812 + 140.95 T / \text{K}$$

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4. Calculate the temperature where the decomposition pressure of limestone (CaCO_3) is 0.6 atm. The following standard Gibbs energies of formation are known, when the substances are formed from their elements:

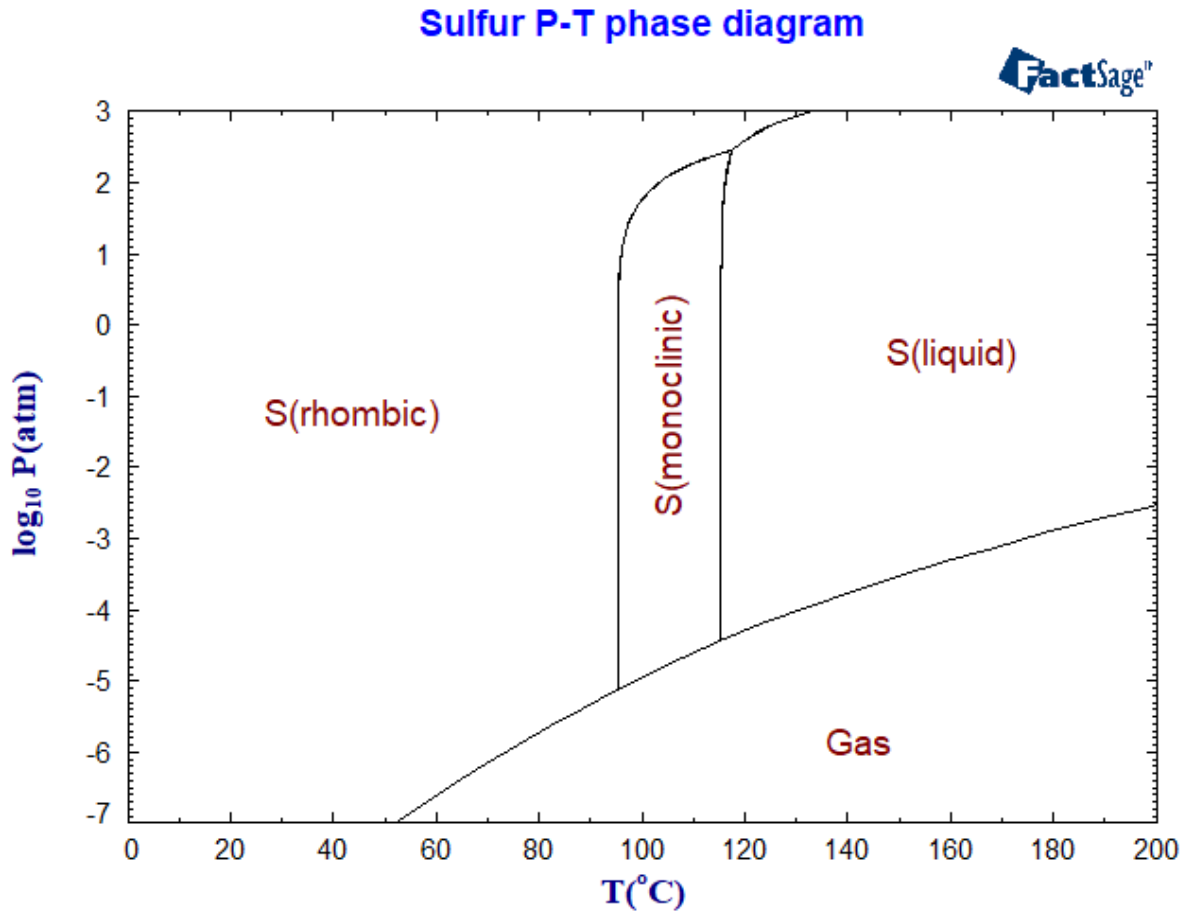
$$\Delta G^\circ(\text{CaO}) = -633123 + 98.99 \cdot T \quad \text{J/mol}$$

$$\Delta G^\circ(\text{CO}_2(\text{g})) = -394133 - 0.80 \cdot T \quad \text{J/mol}$$

$$\Delta G^\circ(\text{CaCO}_3) = -1202984 + 249.62 \cdot T \quad \text{J/mol}$$

5. a) What is the Gibbs phase rule and the meaning of its variables?

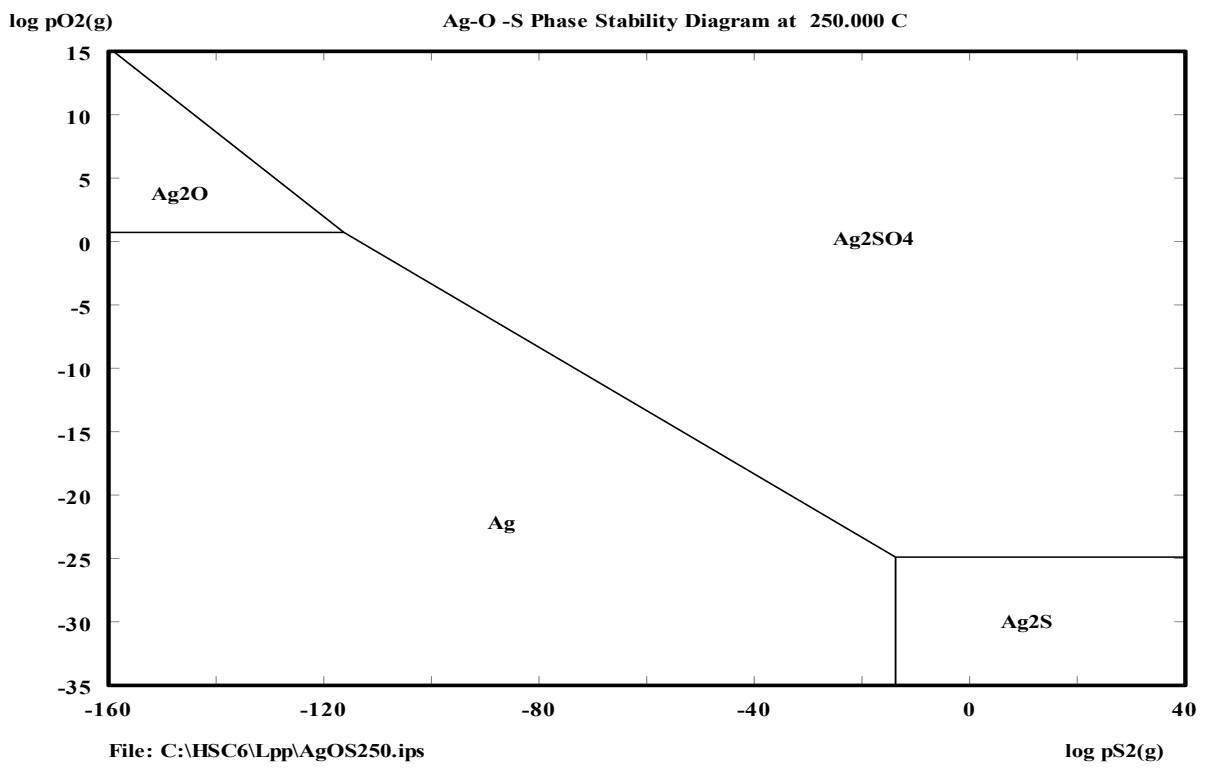
b) Identify the P-T-coordinates for the invariant points in the P-T phase diagram of sulfur below, and identify the stable phases at these invariant points.



6. The included Kellogg diagram shows equilibria and the phase boundaries between pure substances and gas at a constant temperature in system Ag-S-O.

- Write the equilibrium reaction and the Gibbs energy of the reaction for the phase boundary between silver sulfide and silver sulphate.
- Calculate the equilibrium pressure of oxygen at the silver sulfide and silver sulphate phase boundary using the Gibbs energy values given below.
- What is the stable phase at 250 °C when sulfur pressure in the system is $P(S_2) = 10^{-40}$ atm and oxygen pressure is $P(O_2) = 10^{-5}$ atm?

| Reactions | T = 523.15 K | $\Delta G^\circ / \text{J/mol}$ |
|---|--------------|---------------------------------|
| $2\text{Ag} + \frac{1}{2}\text{O}_2(\text{g}) = \text{Ag}_2\text{O}$ | | 3622 |
| $2\text{Ag} + \frac{1}{2}\text{S}_2(\text{g}) = \text{Ag}_2\text{S}$ | | -68903 |
| $2\text{Ag} + \frac{1}{2}\text{S}_2(\text{g}) + 2\text{O}_2(\text{g}) = \text{Ag}_2\text{SO}_4$ | | -567736 |



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Formula Sheet for CHEM-E6100 exam

1. $Z = PV/nRT$
2. $\Delta U = Q - W$
3. $H = U + PV$
4. $C = dQ/dT$
5. $G = H - T \cdot S$
6. $\Delta G = V\Delta P - S\Delta T$
7. $\Delta U = T\Delta S - P\Delta V$
8. $\Delta H = V\Delta P + T\Delta S$
9. $\Delta A = -P\Delta V - S\Delta T$
10. $G(T) = [H^\circ(298K) + \int_{298K}^T c_p \cdot dT] - T \cdot [S^\circ(298K) + \int_{298K}^T \frac{c_p}{T} \cdot dT]$
11. $c_p = a + bT + cT^{-2} + dT^2$
12. $H(T) = [H^\circ(298K) + \left[aT + \frac{1}{2}bT^2 - cT^{-1} + \frac{1}{3}dT^3 \right]_{298K}^T]$
13. $S(T) = \int \frac{c_p}{T} \cdot dT$
14. $\Delta S = \frac{\Delta H}{T}$ (equilibrium)
15. $S(T) = S^\circ(298K) + \left(\int_{298K}^T \frac{a}{T} + b + cT^{-3} + dT \right) dT$
16. $S(T) = S^\circ(298K) + \left[a \ln(T) + bT - \frac{1}{2} cT^{-2} + \frac{1}{2} dT^2 \right]_{298K}^T$
17. $T \cdot S(T) = T \cdot S^\circ(298K) + \left[T \cdot a \ln(T) + bT^2 - \frac{1}{2} cT^{-1} + \frac{1}{2} dT^3 \right]_{298K}^T$
18. $\Delta H_R(T) = \sum \nu \cdot H_i(T)_{products} - \sum \nu \cdot H_i(T)_{reactants}$
19. $\Delta G = -RT \cdot \ln(K)$
20. $K = \frac{\prod a^\nu(products)}{\prod a^\nu(reactants)}$
21. $\Delta G_R(T) = \sum \nu \cdot G_i(T)_{products} - \sum \nu \cdot G_i(T)_{reactants}$
22. $\xi = \frac{n_i - n_{i,0}}{\nu_i}$

NOTE: In formulas 12, 16 and 17 the $]_{298K}^T$ means temperature range 298 K – T K