

The exam **starts at 9:00 and ends at 12:00**, or at 13:00 with a special permit. Your answers must be returned on paper (or, with special permission, to a MyCourses assignment folder). All answers must be written in English.

You may use any materials you find, but do not copy directly from them. The exam must be completed individually, no help from others or online communication is allowed. **The use of AI tools such as ChatGPT, Gemini, etc. is strictly NOT allowed. This also includes AI-generated responses from Google.** Points will be reduced if direct copies are found from sources such as Correction Notes, Wikipedia, textbook, and others. If we suspect the use of AI tools, you may be asked to explain your answers.

The book's appendix tables are needed for the exam. Cite the data source wherever you use data.

1. Carbon-containing molecules are used for fuels, but when burning, they produce CO_2 . Compute how much heat (enthalpy) the following molecules will produce and how much heat is produced per mol of CO_2 . Molecules: graphite C (coal is mostly graphite), methane CH_4 and hexane C_6H_{14} (gasoline contains several hydrocarbons). Write first the reaction equations with O_2 . H_2 would be an excellent fuel, but it is not a natural product. How much heat will be produced in H_2 burning (per mol). All calculations can be done at standard conditions. Explain what you computed. Which of the C-containing molecules is the most ecological fuel? (6 p.)

2. Explain the Carnot Cycle. How the heat, work, and internal energy are consumed or created in each path. What are the total heat, work, and internal energy of the cycle? What is the efficiency of a Carnot heat engine? How is this computed? Compute the efficiency of gasoline and diesel engines. (For gasoline $T_{\text{low}} = 90^\circ\text{C}$, $T_{\text{high}} = 280^\circ\text{C}$, diesel, $T_{\text{low}} = 90^\circ\text{C}$, $T_{\text{high}} = 600^\circ\text{C}$) (6 p.)

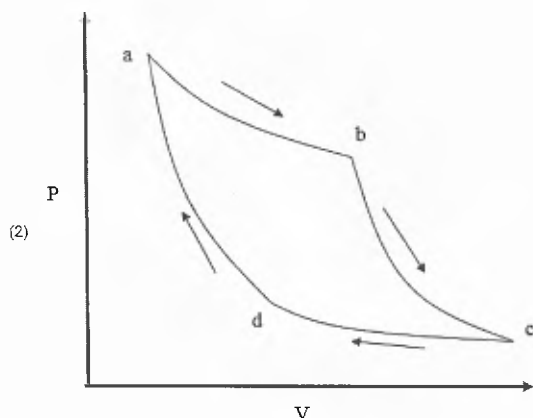


Figure 1: A schematic of P-V diagram for Carnot cycle

3. What the reaction Gibbs energy will tell you about a reaction equilibrium and how it is related to the equilibrium constant at arbitrary pressure. As an example, compute the methanol vapor pressure using thermodynamical data at room temperature ($T = 298.15\text{ K}$, the liquid pressure is 1 atm.) and at 60°C ($T = 333.15\text{ K}$). Explain your calculations. What can you conclude from the 60°C calculations? (6 p.)

4. (a) Explain in your own words what the Clapeyron equation tells us about a P-T phase diagram.
- (b) Use the Clapeyron equation to estimate the slope of the solid-liquid coexistence curve of water at 273 K. Use the parameters below and give the result in bar K⁻¹.
- (c) Explain why the slope of the solid-liquid curve in the P-T phase diagram of water is negative. How does this differ from what is observed for most other substances?
- (d) Predict qualitatively how the melting point of ice changes under an ice skate. Explain briefly.

$$\Delta H_{\text{fusion}} = 6.01 \text{ kJ mol}^{-1}$$

$$\text{Density of ice: } \rho_{\text{ice}} = 0.917 \text{ g cm}^{-3}$$

$$\text{Density of water: } \rho_{\text{water}} = 0.999 \text{ g cm}^{-3}$$

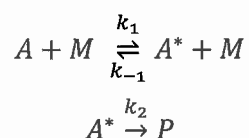
(6 p.)

5. For a binary mixture of liquids A and B forming an ideal solution at 298 K and a total of 1.0 mol of solution:

- (a) Compute ΔG_{mix} , ΔS_{mix} , and ΔH_{mix} for a mixture with $x_A = 0.20$.
- (b) Explain briefly what the signs and magnitudes of ΔG_{mix} , ΔS_{mix} , and ΔH_{mix} mean physically.
- (c) Describe qualitatively how ΔG_{mix} , ΔS_{mix} , and ΔH_{mix} would change if the mixture were non-ideal.
- (d) In many real liquid mixtures of A and B, the molar volume of the solution changes upon mixing ($\Delta V_m < 0$ or $\Delta V_m > 0$). Explain how this can occur in terms of intermolecular interactions.

(6 p.)

6. The unimolecular decomposition of A follows the Lindemann mechanism:



- (a) Write the differential rate equations for A, A* and M. You may assume [M] remains constant during the reaction.
- (b) Explain qualitatively why the intermediate A* does not appear in the final expression for observed rate constant (k_{uni}). See k_{uni} equation below.
- (c) Compute k_{uni} for $[M] = 1.0 \times 10^{-2} \text{ M}$. State whether any simplifying approximation could have been used instead of the full expression for k_{uni} and justify your answer briefly.
- (d) In a separate experiment at $[M] = 5.0 \times 10^{-6} \text{ M}$, the observed half-life of A is $t_{1/2} = 0.029 \text{ s}$. Assume the reaction is first-order to A and calculate the experimentally observed value of k_{uni} . Describe whether the same approximation discussed in part (c) would be valid for this case.

$$k_1 = 5.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$$

$$k_{-1} = 3.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$$

$$k_2 = 5.0 \times 10^5 \text{ s}^{-1}$$

$$k_{\text{uni}} = \frac{k_1 k_2 [M]}{k_{-1} [M] + k_2}$$

(6 p.)