Exam 1

- Answer all questions
- Read all the questions before you begin – answer the easiest ones first
- Show all your work – answers that do not show work will not be given credit
- The exams consists of four questions for a total of 250 points
- Good luck!

Fundamental constants and conversion factors

Gas constant \( R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \)
Boltzmann’s constant \( k_B = 1.381 \times 10^{-23} \text{ J K}^{-1} \)
1 bar = 10\(^5\) Pa
1 atm = 1.01\( \times 10^5\) Pa
Question 1

(a) State the First and Second laws of thermodynamics: (10 points)

First

Second

(b) A real gas at low densities experiences attractive intermolecular interactions. What is the pressure of the real gas compared to the same amount of an ideal gas at the same V, and T. Explain. (10 points)

(c) Using equations, define $C_p$ and $C_V$. Using sketches involving expansion of an ideal gas clearly explain why $C_p > C_V$. (10 points)

(c) Using the compression of an ideal gas as an example distinguish between reversible and irreversible thermodynamics processes. (10 points)
(c) One mole of an ideal gas undergoes a reversible adiabatic compression. Using key equations and by clearly explaining your reasoning, write down the sign of heat \( (q) \) and work \( (w) \). (20 points)

**Question 2**

(a) The internal energy for a solid, liq or an ideal gas changes more dramatically with temperature rather than volume. Using key equations explain the weaker dependence on volume for an ideal gas, and for solids and liquids. [20 points]
(b) Given that \( \left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V - P \), obtain an expression for \( \left( \frac{\partial U}{\partial V} \right)_T \) in terms of isothermal compressibility, \( \kappa \), and isobaric volumetric thermal expansion coefficient, \( \beta \). [20 points]

(c) Enthalpy is given by: \( H = U + PV \). Based on this equation derive a valid Maxwell relation. The following relationship will be useful: \( dU = TdS - PdV \) (20 points)
Question 3
The figure shows a reversible $p$-$V$ Stirling cycle that has been proposed for refrigeration etc. The cycle starts with an ideal gas at a temperature of $T_a$. The gas is isothermally expanded by an input of heat ($q_{ab}$) to position b. The gas contacts a cold reservoir which cools the temperature at constant volume during b to c. Isothermal compression occurs during c to d. Finally the gas is contacted with a hot reservoir to raise its temperature back to $T_a$ during d to a. This occurs at constant volume. Note that only expansion/compression work is possible in this system.

(a) Write down expressions for $q$, $w$, and $\Delta U$ for each stage of the Carnot cycle (24 points)

(b) What is the value of $\Delta U$ for one complete cycle? (6 points)
(c) Write down an expression for the total work for the cycle in terms of the total heat for the cycle. Simplify your expression so that work is expressed in terms of temperature and volume? (20 points)

(d) The efficiency of the Stirling cycle is defined as $\varepsilon = \frac{w_{\text{cycle}}}{q_{ab}}$. Determine an expression for the efficiency of the Stirling heat engine in terms of temperatures. (10 points)
Question 4

Thermodynamic data at 298.15 K:

\[ \Delta H_f^0 (\text{SiH}_4, \text{g}) = 34.3 \text{ kJ mol}^{-1} \]

\[ \Delta H_f^0 (\text{SiO}_2, \text{s}) = -903.49 \text{ kJ mol}^{-1} \]

\[ \Delta H_f^0 (\text{H}_2\text{O}, \text{l}) = -241.818 \text{ kJ mol}^{-1} \]

\[ \Delta G_f^0 (\text{SiH}_4, \text{g}) = 56.9 \text{ kJ mol}^{-1} \]

\[ C_{p,m} (\text{SiH}_4, \text{g}) = 42.84 \text{ J mol}^{-1} \text{ K}^{-1} \]

\[ C_{p,m} (\text{O}_2, \text{g}) = 29.355 \text{ J mol}^{-1} \text{ K}^{-1} \]

\[ C_{p,m} (\text{SiO}_2, \text{s}) = 44.4 \text{ J mol}^{-1} \text{ K}^{-1} \]

\[ C_{p,m} (\text{H}_2\text{O}, \text{g}) = 33.577 \text{ J mol}^{-1} \text{ K}^{-1} \]

(a) Write a Chemical reaction that corresponds to the enthalpy of formation of SiH\textsubscript{4} (g). (10 points)

(b) Using the thermodynamic data determine \( \Delta S_f^0 (\text{SiH}_4, \text{g}). \) (20 points)

(c) Calculate the enthalpy change at 298.15 K for the reaction: \( \text{SiH}_4 (\text{g}) + 2\text{O}_2 (\text{g}) \rightarrow \text{SiO}_2 (\text{s}) + 2\text{H}_2\text{O}(\text{g}) \) (10 points)
(d) Calculate the enthalpy change at 600 K for the reaction: \( \text{SiH}_4(g) + 2\text{O}_2(g) \rightarrow \text{SiO}_2(s) + 2\text{H}_2\text{O}(g) \) (15 points)
(e) Starting from $dU = dq + dw$ derive the Clausius inequality. You must clearly explain your reasoning.

(15 points)