Exercise Classes 1, Physical Chemistry 1 2021/2022

Exercise 1

We consider an isothermal reversible process.
We compress 2.0 mol of a perfect atomic gas isothermally and reversibly from 100 l to 25.0 l at a temperature of 50 °C.

a) Calculate the work W; Is this work done by the surroundings on the system or the other way around?

b) Calculate the heat Q; Is this heat supplied to the system or removed from it? Explain the sign of the result.

Exercise 2

We consider an isochoric reversible process.
We heat 2.0 mol of a perfect atomic gas isochorically and reversibly from 27 °C to 77 °C.

a) Calculate the work; Is this work done by the surroundings on the system or the other way around?

b) Calculate the change in internal energy, ΔU.

Exercise 3

We consider an adiabatic reversible process.
We compress 2.0 mol of a perfect atomic gas adiabatically and reversibly from 100 l to 25.0 l starting at a temperature of 50 °C.

a) First show that for this process $-P\mathrm{d}V = \frac{3}{2}nR\mathrm{d}T$. Hint: Use the internal energy of a perfect atomic gas, $U = \frac{3}{2}nRT$, to find an expression for $\mathrm{d}U$ for a closed system ($\mathrm{d}n = 0$).

b) Then show that, since it is a perfect gas, $-\frac{\mathrm{d}V}{V} = \frac{3}{2}\frac{\mathrm{d}T}{T}$.

c) After that, calculate the final temperature by integrating both sides of the equation of the result of part b) between the limiting values for the state variables in the process.

d) Calculate the work; Explain the difference when comparing the result with exercise 1.

Exercise 4

We consider a non-perfect or real gas, which implies that the equation of state for the gas differs from the perfect gas law. For not too high pressures the equation of state for such a gas can be approximated by a so-called virial expansion of the compression factor $Z \equiv \frac{PV_m}{RT}$ ($V_m = \frac{V}{n}$ is the molar volume):

$$Z = \frac{PV_m}{RT} = \left(1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \frac{D}{V_m^3} + ...\right),$$

where B, C, D are respectively the second, third and fourth (temperature dependent) virial coefficient. In many practical situations we can limit the expansion to the second virial coefficient:

$$\frac{PV_m}{RT} = \left(1 + \frac{B}{V_m}\right).$$

We consider 1 mol argon at temperatures close to 273 K, for which $B = -21.7\ \mathrm{cm^3 mol^{-1}}$ can be considered as independent of T.

The system is subjected to a reversible cyclic process for which we will determine the heat exchange using the first law of thermodynamics.
For that we start from an initial state A characterised by the state variables V_1, P_1, T_1. Next we expand the gas isothermally to V_2 (state B), followed by an isochoric cooling to a temperature T_2 (state C), then an isothermal compression to V_1 (state D) and finally an isochoric heating to T_1.

a) Scetch the cyclic process in a $P-V$-diagram.

b) Express the work W for all four partial processes in terms of the relevante volumes, pressures and temperatures and B.

c) Use the first law to express the net exchanged heat in terms of the state variables and B.

d) Find an expression for the additional heat exchanged due to non-perfect nature of the gas and check whether it increases or decreases.

Exercise 5

We consider an isobaric reversible process.
We heat 2.0 mol of a perfect atomic gas isobarically and reversibly from 27 °C to 77 °C.

a) Calculate the work; Is this work done by the surroundings on the system or the other way around?

b) Calculate the change in internal energy.
Compare the result with that obtained in exercise 2b.