

Tutorials 1 Thermodynamics 2, 2023/2024

Exercise 1

Consider a perfect gas of N CO₂-molecules, which therefore behaves according to the equipartition theorem.

- How many translational and rotational degrees of freedom does the molecule as a whole have?
- Each degree of freedom of the molecule (translational, rotational, vibrational) in fact comes from the specific translations of the individual atoms in the molecule. What is the total number of degrees of freedom for a CO₂-molecule?
- What is therefore the number of vibrational degrees of freedom for a CO₂-molecule?
- Determine the internal energy per mole for the gas at $T = 1000$ K.
- Determine the enthalpy per mole for the gas at $T = 1000$ K.
- Determine the molar heat capacity c_V of the gas at $T = 2000$ K.
- Determine the molar heat capacity c_P of the gas at $T = 2000$ K. Compare these values with the data in the resource section of Atkins.

Exercise 2

State functions.

A state function is a function $f(x, y, z, \dots)$ of independent variables x, y, z, \dots for which the function has an unambiguous value for each of the combinations of variables x, y, z, \dots . A function $f(x, y)$ of two independent variables is a state function if the following holds

$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x} \quad \text{or} \quad \left(\frac{\partial f}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial f}\right)_x = -1.$$

Consider the function $g(x, y) = \ln(xy^2) - x^2y^3$.

- Examine if $g(x, y)$ is a state function.
- Write $dg(x, y)$ as a total differential, so as $dg(x, y) = g_x dx + g_y dy$ and find an expression for $g_x(x, y)$ and $g_y(x, y)$.
- Find a Maxwell relation between $g_x(x, y)$ and $g_y(x, y)$ and check that the Maxwell relation indeed holds.
- We rewrite the Maxwell relation as

$$dg_x = \frac{\partial g_y}{\partial x} dy, \quad \text{and} \quad dg_y = \frac{\partial g_x}{\partial y} dx.$$

Calculate Δg between $(x, y) = (1, 2)$ and $(x, y) = (4, 3)$ by integrating $dg(x, y)$ first at constant y and subsequently at constant x , and alternatively, first at constant x and subsequently at constant y , which should give the same result.

Hint: use the total differential of $g(x, y)$ for that and the fact that for constant x we can use $dx = 0$ and for constant y , $dy = 0$ holds.

Exercise 3

- Write down the characteristic equations for dU , dH , dA and dG for an electrical cell as a closed system, by adding the additional electrical work term Edq , in which E is the EMF (electromotive force, or cell potential, or preferably: cell voltage) and dq is the charge transferred.
- Determine all Maxwell-relations that you can derive from these equations.
- Determine the characteristic equations for dU , dH , dA and dG for an electrical cell as an open system, by adding also the term μdn . Assume that there is only one type of particle present in the cell.
- Determine all the Maxwell-relations that you can derive from the resulting equation for the Gibbs free energy.

Exercise 4

In this exercise we will practice the use of state functions and total differentials. We will derive the following *thermodynamic equation of state*:

$$\left(\frac{\partial H}{\partial T}\right)_V = \left(1 - \frac{\alpha\mu}{\kappa_T}\right) C_P,$$

in which four experimentally measurable quantities occur.

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P \quad \text{the coefficient of thermal expansion,}$$

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H \quad \text{the Joule-Thomson coefficient,}$$

not to be confused with the chemical potential

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T \quad \text{the isothermal compressibility}$$

and the already familiar

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \quad \text{the isobaric heat capacity.}$$

With the above expression, we can measure the dependence of the enthalpy on the temperature at constant volume for any closed system.

- To derive the thermodynamic equation of state, consider the enthalpy, in contrast to what you are used to, as a function of P and T and determine the total differential. If you find this peculiar, you might want to read appendix A of the study guide.
- Differentiate the result of part a) with respect to T at constant V .
- Use the relation between the variables of state functions (Atkins (ed. 11), page 44, or page 109 till 111 (ed. 10), or page 91-31 (ed. 9), or Appendix 2.6 (ed. 8)) to rewrite the last expression of part b) to the experimental variables as defined above to find the thermodynamic equation of state.