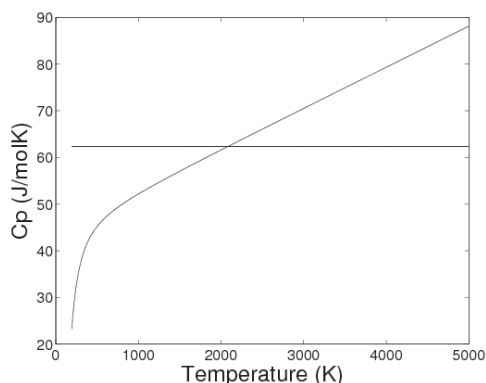


Answers Tutorials 1 Thermodynamics 2, 2023/2024

Exercise 1

- a) There are always three translational degrees of freedom (x, y, z) per molecule in three dimensions. Since CO_2 is a linear molecule, there are two axes of rotation, so two degrees of rotational freedom per molecule. For this gas we thus have $N^T = 3N$ and $N^R = 2N$.
- b) Each CO_2 -molecule consists of three atoms with each three (translational) degrees of freedom, which gives us a total of nine degrees of freedom per molecule: $N^{\text{tot}} = 9N$.
- c) N^{tot} consists of N^T , N^R and the contribution of vibrational modes N^V , therefore $N^V = N^{\text{tot}} - N^T - N^R = 9N - 3N - 2N = 4N$. N.b., For a translation of the entire molecule the movements of the three atoms are equal. For the two rotational modes, the oxygen atoms rotate around the carbon atom. For one of the vibrational modes, the oxygen atoms move opposite of each other along the axis of the molecule. For the other vibrational modes, the movements are somewhat more complex.
- d) The internal energy is $\frac{1}{2}kT$ per degree of freedom according to the equipartition theorem. The rotational and translational modes have one degree of freedom and the vibrational modes have two (kinetic and potential energy).
 $U = \frac{1}{2} (N^T + N^R + 2N^V) kT = \frac{1}{2} (3N + 2N + 2 \cdot 4N) kT = \frac{13}{2} NkT$ for the entire gas or $\frac{13}{2} RT = \frac{13}{2} 8.314 \cdot 1000 = 54.04 \text{ kJmol}^{-1}$.
- e) $H = U + PV$, which for a perfect gas, using the equation of state, implies $H = U + nRT$, which means that the molar enthalpy equals $H = \frac{15}{2} RT = \frac{15}{2} \cdot 8.314 \cdot 1000 = 62.36 \text{ kJmol}^{-1}$.
N.b the PV -term is not affected by the rotations and vibrations at the high temperatures of the equipartition theorem because their (quantum mechanical) energy levels are independent of V , as opposed to the translations. Therefore $PV = nRT$ remains valid.
- f) $c_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{13}{2} R = 54.04 \text{ Jmol}^{-1}\text{K}^{-1}$, independent of the temperature! This only applies to a perfect gas.
- g) $c_P = \left(\frac{\partial H}{\partial T}\right)_P = \frac{15}{2} R = 62.36 \text{ Jmol}^{-1}\text{K}^{-1}$, independent of the temperature! This again only applies to a perfect gas.
The $c_P(CO_2) = 44.22 + 8.79 \cdot 10^{-3}T - 8.62 \cdot 10^{-5}T^{-2} \text{ Jmol}^{-1}\text{K}^{-1}$ according to Atkins table 2B.1 (ed. 11). At a temperature of $T = 2000 \text{ K}$ that would give a value of $c_P(CO_2, 2000\text{K}) = 44.22 + 8.79 \cdot 2 - 8.62/40 = 61.58 \text{ Jmol}^{-1}\text{K}^{-1}$, which is smaller than the result of the equipartition theorem. The c_P as function of temperature is plotted in the figure below (from the boiling point of 195 K) for both the equipartition value and data from Atkins; for the latter we silently (and certainly falsely) assumed that this data is valid for the entire temperature range of the plot.



Exercise 2

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

a) $g(x, y)$ is a state function if

$$\frac{\partial^2 g}{\partial x \partial y} = \frac{\partial^2 g}{\partial y \partial x}$$

Checking this gives

$$\frac{\partial^2 g}{\partial x \partial y} = \frac{\partial}{\partial x} \left(\frac{\partial g}{\partial y} \Big|_x \right) \Big|_y = \frac{\partial}{\partial x} \left(\frac{1}{xy^2} 2xy - 3x^2y^2 \right) \Big|_y = \frac{\partial}{\partial x} \left(\frac{2}{y} - 3x^2y^2 \right) \Big|_y = -6xy^2, \text{ and}$$

$$\frac{\partial^2 g}{\partial y \partial x} = \frac{\partial}{\partial y} \left(\frac{\partial g}{\partial x} \Big|_y \right) \Big|_x = \frac{\partial}{\partial y} \left(\frac{\partial g}{\partial x} \Big|_y \right) \Big|_x = \frac{\partial}{\partial y} \left(\frac{1}{xy^2} y^2 - 2xy^3 \right) \Big|_x = \frac{\partial}{\partial y} \left(\frac{1}{x} - 2xy^3 \right) \Big|_x = -6xy^2$$

These results are the same, so we are dealing with a state function.

b) The total differential of $g(x, y)$ is $dg(x, y) = g_x dx + g_y dy$, with

$$g_x(x, y) = \frac{\partial g}{\partial x} \Big|_y = \frac{1}{x} - 2xy^3, \text{ and } g_y(x, y) = \frac{\partial g}{\partial y} \Big|_x = \frac{2}{y} - 3x^2y^2, \text{ so}$$

$$dg(x, y) = \left(\frac{1}{x} - 2xy^3 \right) dx + \left(\frac{2}{y} - 3x^2y^2 \right) dy.$$

c) The Maxwell relation between $g_x(x, y)$ and $g_y(x, y)$ is

$$\frac{\partial g_x}{\partial y} \Big|_x = \frac{\partial g_y}{\partial x} \Big|_y, \text{ so}$$

$$\frac{\partial \left(\frac{1}{x} - 2xy^3 \right)}{\partial y} \Big|_x = \frac{\partial \left(\frac{2}{y} - 3x^2y^2 \right)}{\partial x} \Big|_y,$$

which worked out leads to

$$-6xy^2 = -6xy^2,$$

which shows that the Maxwell relation indeed holds.

d) We rewrite the Maxwell relation as

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

The total differential of $g(x, y)$ is $dg(x, y) = g_x dx + g_y dy$.

To determine Δg_x between $(x, y) = (1, 2)$ and $(x, y) = (4, 3)$ by integrating $g(x, y)$ first at constant y and subsequently at constant x we find

$$\begin{aligned} \Delta g &= \int_{(1,2)}^{(4,3)} dg(x, y) = \int_{(1,2)}^{(4,2)} g_x(x, y) dx + \int_{(4,2)}^{(4,3)} g_y(x, y) dy \\ &= \int_{(1,2)}^{(4,2)} \left(\frac{1}{x} - 2xy^3 \right) dx + \int_{(4,2)}^{(4,3)} \left(\frac{2}{y} - 3x^2y^2 \right) dy = [\ln(x) - x^2y^3]_{(1,2)}^{(4,2)} + [2 \ln(y) - x^2y^3]_{(4,2)}^{(4,3)} \\ &= (\ln 4 - 4^2 \cdot 2^3) - (\ln 1 - 1^2 \cdot 2^3) + (2 \ln 3 - 4^2 \cdot 3^3) - (2 \ln 2 - 4^2 \cdot 2^3) \\ &= (2 \ln 2 - 128) - (0 - 8) + (2 \ln 3 - 432) - (2 \ln 2 - 128) = 2 \ln \frac{2 \cdot 3}{2} - 324 = 2 \ln 3 - 324. \end{aligned}$$

The alternative integration path gives

$$\begin{aligned}
 \Delta g &= \int_{(1,2)}^{(4,3)} dg(x,y) = \int_{(1,2)}^{(1,3)} g_y(x,y)dy + \int_{(1,3)}^{(4,3)} g_x(x,y)dx \\
 &= \int_{(1,2)}^{(1,3)} \left(\frac{2}{y} - 3x^2y^2 \right) dy + \int_{(1,3)}^{(4,3)} \left(\frac{1}{x} - 2xy^3 \right) dx = [2 \ln y - x^2y^3]_{(1,2)}^{(1,3)} + [\ln x - x^2y^3]_{(1,3)}^{(4,3)} \\
 &= (2 \ln 3 - 1^2 \cdot 3^3) - (2 \ln 2 - 1^2 \cdot 2^3) + (\ln 4 - 4^2 \cdot 3^3) - (\ln 1 - 1^2 \cdot 3^3) \\
 &= 2 \ln 3 - 324.
 \end{aligned}$$

This indeed gives the same result, which should be the case for a state function.

NOTE: It is important to note that the partial derivatives $g_x(x,y)$ and $g_y(x,y)$ are still a function of both x and y , and their dependencies should be taken into account when integrating, as we did!

Exercise 3

- a) The non-expansion work of the electrical cell is $dW' = Edq$, in which E is the EMF (electromotive force, or cell potential, or preferably: cell voltage) and dq is the charge transferred.

For the characteristic equations we find

$$dU = -PdV + TdS + Edq$$

$$dH = VdP + TdS + Edq$$

$$dA = -PdV - SdT + Edq$$

$$dG = VdP - SdT + Edq$$

- b) The first Maxwell-relation in the table below follows from

$$\left(\frac{\partial^2 U}{\partial S \partial V} \right)_q = \left(\frac{\partial^2 U}{\partial V \partial S} \right)_q \quad \text{so} \quad \left(\frac{\partial(-P)}{\partial S} \right)_{V,q} = \left(\frac{\partial T}{\partial V} \right)_{S,q}$$

| | | | |
|---|---|---|---|
| U | $\left(\frac{\partial P}{\partial S} \right)_{V,q} = - \left(\frac{\partial T}{\partial V} \right)_{S,q}$ | $\left(\frac{\partial P}{\partial q} \right)_{V,S} = - \left(\frac{\partial E}{\partial V} \right)_{S,q}$ | $\left(\frac{\partial T}{\partial q} \right)_{V,S} = \left(\frac{\partial E}{\partial S} \right)_{V,q}$ |
| H | $\left(\frac{\partial V}{\partial S} \right)_{P,q} = \left(\frac{\partial T}{\partial P} \right)_{S,q}$ | $\left(\frac{\partial V}{\partial q} \right)_{P,S} = \left(\frac{\partial E}{\partial P} \right)_{S,q}$ | $\left(\frac{\partial T}{\partial q} \right)_{P,S} = \left(\frac{\partial E}{\partial S} \right)_{P,q}$ |
| A | $\left(\frac{\partial P}{\partial T} \right)_{V,q} = \left(\frac{\partial S}{\partial V} \right)_{T,q}$ | $\left(\frac{\partial P}{\partial q} \right)_{V,T} = - \left(\frac{\partial E}{\partial V} \right)_{T,q}$ | $\left(\frac{\partial S}{\partial q} \right)_{V,T} = - \left(\frac{\partial E}{\partial T} \right)_{V,q}$ |
| G | $\left(\frac{\partial V}{\partial T} \right)_{P,q} = - \left(\frac{\partial S}{\partial P} \right)_{T,q}$ | $\left(\frac{\partial V}{\partial q} \right)_{P,T} = \left(\frac{\partial E}{\partial P} \right)_{T,q}$ | $\left(\frac{\partial S}{\partial q} \right)_{P,T} = - \left(\frac{\partial E}{\partial T} \right)_{P,q}$ |

- c) For an open system with one type of particle we need an extra term μdn , in which μ is the chemical potential. For the characteristic equations we find

$$dU = -PdV + TdS + Edq + \mu dn$$

$$dH = VdP + TdS + Edq + \mu dn$$

$$dA = -PdV - SdT + Edq + \mu dn$$

$$dG = VdP - SdT + Edq + \mu dn$$

- d) The Maxwell-relations that follow from the equation for the Gibbs free energy can be found in the following overview. The three in the top row are the same as those in part b), besides being at constant n . The other three are new relations for an open system.

| | | |
|---|---|---|
| $\left(\frac{\partial V}{\partial T} \right)_{P,q,n} = - \left(\frac{\partial S}{\partial P} \right)_{T,q,n}$ | $\left(\frac{\partial V}{\partial q} \right)_{P,T,n} = \left(\frac{\partial E}{\partial P} \right)_{T,q,n}$ | $\left(\frac{\partial S}{\partial q} \right)_{P,T,n} = - \left(\frac{\partial E}{\partial T} \right)_{P,q,n}$ |
| $\left(\frac{\partial V}{\partial n} \right)_{P,T,q} = \left(\frac{\partial \mu}{\partial P} \right)_{T,q,n}$ | $\left(\frac{\partial S}{\partial n} \right)_{P,T,q} = - \left(\frac{\partial \mu}{\partial T} \right)_{P,q,n}$ | $\left(\frac{\partial E}{\partial n} \right)_{P,T,q} = \left(\frac{\partial \mu}{\partial q} \right)_{P,T,n}$ |

Exercise 4

- a) We would normally write the enthalpy as a function of P and S , which gives the total differential

$$dH = \left(\frac{\partial H}{\partial P}\right)_S dP + \left(\frac{\partial H}{\partial S}\right)_P dS, \quad \text{with} \quad \left(\frac{\partial H}{\partial P}\right)_S = V \quad \text{and} \quad \left(\frac{\partial H}{\partial S}\right)_P = T,$$

the latter equations following from the characteristic equation for the enthalpy: $dH = TdS + VdP$. Now we consider $H = H(P, T)$, which leads to the total differential

$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP + \left(\frac{\partial H}{\partial T}\right)_P dT.$$

If you find this peculiar, you might want to read appendix A of the study guide.

- b) We take the partial derivative of the result of a) with respect to T at constant V :

$$\left(\frac{\partial H}{\partial T}\right)_V = \left(\frac{\partial H}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V + \left(\frac{\partial H}{\partial T}\right)_P.$$

N.B.: $\left(\frac{\partial H}{\partial P}\right)_T$ and $\left(\frac{\partial H}{\partial T}\right)_P$ are coefficients in the total differential of $H(P, T)$, and can therefore be considered as parameters when determining the derivative $\left(\frac{\partial H}{\partial T}\right)_V$.

- c) First of all we recognize

$$\left(\frac{\partial H}{\partial T}\right)_P = C_P.$$

We use the following relations for exact differentials of state functions (Atkins: Appendix 2.6 (ed. 8) c.q. page 91-31 (ed. 9) c.q. page 109 till 111 (ed. 10) c.q. page 44 (ed. 11)):

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z} \quad \text{and}$$

$$\left(\frac{\partial x}{\partial y}\right)_z = - \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x,$$

implying

$$\left(\frac{\partial H}{\partial P}\right)_T = - \left(\frac{\partial H}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_H = -\mu C_P$$

and

$$\left(\frac{\partial P}{\partial T}\right)_V = - \left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P = - \frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T} = \frac{V\alpha}{V\kappa_T} = \frac{\alpha}{\kappa_T}.$$

When we combine these results we find

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