Answers Tutorials 1 Thermodynamics 2, 2025/2026

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 of N molecules 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. For N molecules we thus have $N^{\text{tot}} = 9N$.

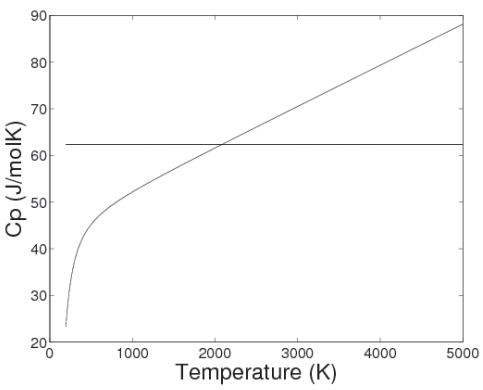
c) N^{tot} consists of N^T, N^R and the contribution of vibrational modes N^V, therefore $N^V = N^{\text{tot}} - N^T - N^R = 9N - 3N - 2N = 4N$. N.b., For a translation of the entire molecule the movements of the three atoms are equal. For the two rotational modes, the oxygen atoms rotate around the 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).
$U = \left(N^T + N^R + 2N^V\right)\frac{1}{2}kT = (3N + 2N + 2 \cdot 4N)\,\frac{1}{2}kT = \frac{13}{2}NkT$ for the entire gas or $\frac{13}{2}RT = \frac{13}{2}8.314 \cdot 1000 = 54.04$ 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 $H = \frac{15}{2}RT = \frac{15}{2} \cdot 8.314 \cdot 1000 = 62.36$ 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) $c_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{13}{2}R = 54.04$ Jmol^{-1}K^{-1}, independent of the temperature! This only applies to a perfect gas.

g) $c_P = \left(\frac{\partial H}{\partial T}\right)_P = \frac{15}{2}R = 62.36$ Jmol^{-1}K^{-1}, independent of the temperature! This only applies to a perfect gas, so for high enough temperature and (still) low pressure.
Atkins' table 2B.1 (ed. 11 or 12) gives $c_P(CO_2) = 44.22 + 8.79 \cdot 10^{-3}\text{T} - 8.62 \cdot 10^5\text{T}^{-2}$ Jmol^{-1}K^{-1}. At a temperature of $T = 2000$ K that would give a value of $c_P(CO_2, 2000\text{K}) = 44.22 + 8.79 \cdot 2 - 8.62/40 = 61.58$ Jmol^{-1}K^{-1}, which is smaller then the result of the equipartition theorem. 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 Atkins' expression is valid for the entire temperature range of the plot.



Exercise 2

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

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

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

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

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

b) The total differential of $g(x,y)$ is $\mathrm{d}g(x,y) = g_x\mathrm{d}x + g_y\mathrm{d}y$, with

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

$$\mathrm{d}g(x,y) = \left(\frac{1}{x} - 2xy^3\right)\mathrm{d}x + \left(\frac{2}{y} - 3x^2y^2\right)\mathrm{d}y.$$

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

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

which worked out leads to

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

which shows that the Maxwell relation indeed holds.

d) The total differential of $g(x,y)$ is $\mathrm{d}g(x,y) = g_x\mathrm{d}x + g_y\mathrm{d}y$.
To determine Δg 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

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

The alternative integration path gives

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

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 $\mathrm{d}W' = E\mathrm{d}q$, in which E is the EMF (electromotive force, or cell potential, or preferably: cell voltage) and $\mathrm{d}q$ is the charge transfered.
For the characteristic equations we find
$\mathrm{d}U = -P\mathrm{d}V + T\mathrm{d}S + E\mathrm{d}q$
$\mathrm{d}H = V\mathrm{d}P + T\mathrm{d}S + E\mathrm{d}q$
$\mathrm{d}A = -P\mathrm{d}V - S\mathrm{d}T + E\mathrm{d}q$
$\mathrm{d}G = V\mathrm{d}P - S\mathrm{d}T + E\mathrm{d}q$

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 $\mu\mathrm{d}n$, in which μ is the chemical potential. For the characteristic equations we find
$\mathrm{d}U = -P\mathrm{d}V + T\mathrm{d}S + E\mathrm{d}q + \mu\mathrm{d}n$
$\mathrm{d}H = V\mathrm{d}P + T\mathrm{d}S + E\mathrm{d}q + \mu\mathrm{d}n$
$\mathrm{d}A = -P\mathrm{d}V - S\mathrm{d}T + E\mathrm{d}q + \mu\mathrm{d}n$
$\mathrm{d}G = V\mathrm{d}P - S\mathrm{d}T + E\mathrm{d}q + \mu\mathrm{d}n$

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) For a perfect gas we found in the lecture and in exercise 1 that the internal energy is given by $U = \left(N^T + N^R + 2N^V\right)\frac{1}{2}kT$, where N^T, N^R and N^V are constants depending on the type of molecules. Therefore, the internal energy depends only on the temperature T and, thus

$$\Pi_T = \left(\frac{\partial U}{\partial V}\right)_T = 0.$$

b) Using the total differential of U

$$\mathrm{d}U(S,V) = \left(\frac{\partial U}{\partial S}\right)_V \mathrm{d}S + \left(\frac{\partial U}{\partial V}\right)_S \mathrm{d}V,$$

we find (note that the partial derivatives in the total differential are coefficients of $U(S,V)$ and can therefore be considered as parameters when determining the partial derivative $\left(\frac{\partial U}{\partial V}\right)_T$)

$$\Pi_T = \left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial U}{\partial S}\right)_V \left(\frac{\partial S}{\partial V}\right)_T + \left(\frac{\partial U}{\partial V}\right)_S \left(\frac{\partial V}{\partial V}\right)_T,$$

c) The characteristic equation for U is $dU(S,V) = TdS - PdV$, so we can replace the partial derivatives in the total differential of $U(S,V)$ in part b) by respectively T and $-P$:

$$\Pi_T = \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P\left(\frac{\partial V}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P.$$

To get rid of the partial derivative with the entropy S, we use the Maxwell relation (obtained from the Helmholtz free energy; see also exercise 3b))

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V,$$

to finally obtain

$$\Pi_T = \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P.$$

d) Applying this result to a van de Waals gas with equation of state

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2},$$

we find

$$\Pi_T = T\frac{nR}{V - nb} - \left(\frac{nRT}{V - nb} - \frac{n^2 a}{V^2}\right) = \frac{n^2 a}{V^2}.$$

With the value of $a = 3.610$ atm dm^6 mol^{-2} $= 3.610 \cdot 1.01325 \cdot 10^5 \cdot 10^{-6} = 0.3658$ Pa m^6 mol^{-2} and $n = 2$ mol, we find $\Pi_T = \frac{2^2 \cdot 0.3658}{V^2} = \frac{1.463}{V^2}$ Pa.
With the definition of $\Pi_T = \left(\frac{\partial U}{\partial V}\right)_T$ we can determine the change in internal energy as a result of an isothermal compression of the gas:

$$\Delta U_T = \int \Pi_T \mathrm{d}V = n^2 a \int_{V_1}^{V_2} \frac{\mathrm{d}V}{V^2} = -n^2 a \left[\frac{1}{V}\right]_{V_1}^{V_2} = -n^2 a \left(\frac{1}{V_2} - \frac{1}{V_1}\right),$$

which gives on plugging in the values

$$\Delta U_T = -1.463 \left(\frac{1}{200 \cdot 10^{-3}} - \frac{1}{400 \cdot 10^{-3}}\right) = -3.66 \text{ J}.$$

To give an impression of the deviation from ideal behaviour we calculate the internal energy in case of a perfact gas behaviour for CO_2 (use the result of exercise 1d):

$$U^{\text{perfect gas}} = \frac{13}{2} nRT = \frac{13}{2} 2 \cdot 8.314 \cdot 2000 = 2.16 \cdot 10^5 \text{ J},$$

independent of temperature. The relative deviation is $\frac{-3.66}{2.16 \cdot 10^5} = -1.7 \cdot 10^{-5} \approx -0.02$ ‰, so very small, even at the rather low final pressure of

$$P \approx P^{\text{perfect gas}} = \frac{nRT}{V} = \frac{2 \cdot 8.314 \cdot 2000}{200 \cdot 10^{-3}} = 66 \cdot 10^3 \text{ Pa} = 0.66 \text{ bar}.$$