Solutions Exercise Classes 2, Physical Chemistry 1 2021/2022

Exercise 6

a) Isothermal so $\Delta T = 0$, hence

• $T_2 = T_1 = 298$ K.

Moreover, it is a perfect gas so (reversible so $P_{ext.} = P$; furthermore $n = 1$ mol)

$W = -\int_{V_1}^{V_2} P \mathrm{d}V = -RT \int_{V_1}^{V_2} \frac{\mathrm{d}V}{V} = -RT \ln \frac{V_2}{V_1} = -RT \ln \frac{P_1}{P_2} = -8.31 \cdot 298 \ln \frac{5.0}{1.0} = -4.0$ kJ, so

• $W = -4.0$ kJ, so the system does work on the surroundings.

Perfect gas so U only depends on T; also isothermal hence

•$\Delta U = 0$.

$\Delta U = W + Q = 0$, so

• $Q = 4.0$ kJ.

Reversible process so $Q_{rev} = Q$.

Isothermal so $\Delta S = \int \frac{\mathrm{d}Q_{rev}}{T} = \frac{1}{T} \int \mathrm{d}Q = \frac{Q}{T} = \frac{4.0 \cdot 10^3}{298} = 13.4$ JK^{-1}, therefore

• $\Delta S = 13.4$ JK^{-1}.

$A \equiv U - TS$. Thus at constant T we find $\Delta A = \Delta U - T\Delta S = 0 - 298 \cdot 13.4 = -4.0$ kJ, so

• $\Delta A = -4.0$ kJ.

$G \equiv H - TS$. So for constant T we find $\Delta G = \Delta H - T\Delta S$. For a perfect gas H only depends on T so $\Delta H = 0$, such that

• $\Delta G = -T\Delta S = -4.0$ kJ.

b) • State functions.

The change in a state function (conserved quantity) is independent of the path taken during a process and is only determined by the initial and the final state. Both processes are isothermal and also have the same final pressure such that (n is constant) due to the equation of state (perfect gas, so $PV = nRT$) also the final volume must be equal for both processes.

So also the final states are equal for both processes. U, H, A, G and S are state functions, so ΔU, ΔH, ΔA, ΔG and ΔS must be equal for both processes.

• Non state functions.

Q and W are not state functions. Since Q will be different for the two processes, also the entropy change for the surroundings will be different.

c) We therefore only have to consider W and Q for the irreversible process.

Isothermal so $\Delta T = 0$, such that still $T_2 = T_1 = 298$ K. Moreover, the final pressure of the gas is $P_2 = P_{ext}$ and P_{ext} is constant during the process.

For the work (not reversible so $P_{ext.} \neq P_{gas}$) we need to return to the definition

$W = -\int_{V_1}^{V_2} P_{ext.} \mathrm{d}V = -P_{ext.} \int_{V_1}^{V_2} \mathrm{d}V = -P_{ext.} \Delta V = -P_2(V_2 - V_1) = -RT + P_2 \frac{RT}{P_1} = -RT \left(1 - \frac{P_2}{P_1}\right) = -8.31 \cdot 298 \left(1 - \frac{1.0}{5.0}\right) = -2.0$ kJ, so

• $W = -2.0$ kJ.

So the work done by the gas on the surroundings ($W < 0$) is smaller for the irreversible process. We already found that $\Delta U = 0$, such that $Q = -W$, therefore

• $Q = 2.0$ kJ.

This implies that, due to the constant internal energy of the perfect gas at constant T, the heat absorbed by the gas from the surroundings (the bath) is smaller for the irreversible process. The entropy of the surroundings, therefore, decreases less ($\Delta S_{env} = -\frac{Q}{T}$) for the irreversible process. The smaller value for the heat also serves as an example for the Clausius inequality as a formulation of the second law:

$$dQ \leq TdS, \text{ with } \quad dQ^{rev} \equiv TdS, \text{ so } \quad dQ^{irr} < dQ^{rev} \quad \text{and} \quad Q^{irr} < Q^{rev}.$$

Exercise 7

a) Adiabatic so $Q = 0$.
In vacuum so $P_{ext.} = 0 \Rightarrow \mathrm{d}W = -P_{ext.}\mathrm{d}V = 0$, even though the volume increases.
Thus $\Delta U = W + Q = 0$; perfect gas so $U = U(T)$, with $\mathrm{d}U = 0$, so $\mathrm{d}T = 0$, and $T_2 = T_1$.
Apparently the gas expands isothermally such that $P_1V_1 = nRT$ and $P_2V_2 = nRT$ or $P_1V_1 = P_2V_2$.

b) S is a state function, so to determine $\Delta S \equiv \int \frac{\mathrm{d}Q^{rev}}{T}$ we can choose an alternative reversible path as in Figure 1, for which $\Delta S_{AB} = \Delta S_{AC} + \Delta S_{CB}$.
—Process AC is reversible, so $\mathrm{d}Q^{rev} = \mathrm{d}Q = \mathrm{d}U - \mathrm{d}W = \mathrm{d}U + P_{ext.}\mathrm{d}V = \mathrm{d}U + P\mathrm{d}V$.

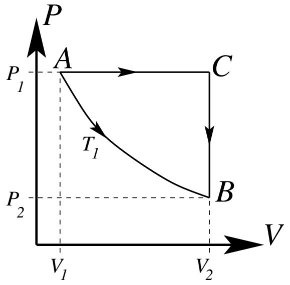

Figure 1: AB is the *irreversible* process; ACB is the alternative path with AC a *reversible* isobaric expansion and CB a *reversible* isochoric pressure decrease. Note: the temperature is only constant on the isotherm AB.

Also isobaric, so $\mathrm{d}P = 0$. Therefore, the enthalpy H becomes a suitable energy function:
$\mathrm{d}H \equiv \mathrm{d}U + \mathrm{d}(PV) = \mathrm{d}U + P\mathrm{d}V + V\mathrm{d}P = \mathrm{d}U + P\mathrm{d}V = \mathrm{d}Q - P\mathrm{d}V + P\mathrm{d}V = \mathrm{d}Q$.
Therefore $\mathrm{d}Q^{rev} = \mathrm{d}Q = \mathrm{d}H = C_P\mathrm{d}T$, because $\left(\frac{\partial H}{\partial T}\right)_P \equiv C_P$.
For a perfect gas C_P (and also C_V) is independent of the temperature, so the entropy change of the path AC is equal to $\Delta S_{AC} = \int_{T_1}^{T_C} \frac{\mathrm{d}Q^{rev}}{T} = \int_{T_1}^{T_C} \frac{C_P\mathrm{d}T}{T} = C_P \ln \frac{T_C}{T_1}$.
—Process CB is isochoric, so $\mathrm{d}V = 0$ and the internal energy U becomes a suitable energy function.
$\mathrm{d}U = \mathrm{d}Q - P\mathrm{d}V = \mathrm{d}Q^{rev} - P\mathrm{d}V = \mathrm{d}Q^{rev}$, since CB is reversible and isochoric.
The entropy change is therefore $\Delta S_{CB} = \int_{T_C}^{T_2} \frac{\mathrm{d}Q^{rev}}{T} = \int_{T_C}^{T_2} \frac{C_V\mathrm{d}T}{T} = C_V \ln \frac{T_2}{T_c}$.
—Thus we find in total $\Delta S_{AB} = \Delta S_{AC} + \Delta S_{CB} = C_V \ln \frac{T_2}{T_C} + C_P \ln \frac{T_C}{T_1}$.
Earlier we found $T_2 = T_1 \equiv T$, so $\Delta S_{AB} = C_V \ln \frac{T}{T_C} + C_P \ln \frac{T_C}{T} = (C_V - C_P) \ln \frac{T}{T_C}$.
T_C follows from the equation of state applied at the state C, where $P_1V_2 = nRT_C$.
Using $nRT = P_1V_1 = P_2V_2$ it follows that
$\Delta S_{AB} = (C_V - C_P) \ln \frac{nRT}{P_1V_2} = (C_V - C_P) \ln \frac{P_1V_1}{P_1V_2} = (C_V - C_P) \ln \frac{V_1}{V_2}$.
If we limit ourselves to a perfect gas of *atoms*, then for the heat capacities we have $C_V = \frac{3}{2}nR$ and $C_P = \frac{5}{2}nR$, such that $\Delta S_{AB} = (\frac{3}{2} - \frac{5}{2})nR \ln \frac{V_1}{V_2} = -nR \ln \frac{V_1}{V_2} = nR \ln \frac{V_2}{V_1}$.
This expression holds for both an atomic gas as well as a molecular perfect gas, since the vibrations and rotations of molecules do not contribute to the difference term $H - U = PV$.

Allthough the suggested solution has the didactical advantage of illustrating the use of an alternative path to determine the change of a state function, the result can be obtained much easier by sticking to the original isotherm, and only performing the expansion reversibly.
Then the latter condition ensures that $\mathrm{d}S \equiv \frac{\mathrm{d}Q^{rev}}{T} = \frac{\mathrm{d}Q}{T}$, and the first condition ($\mathrm{d}T = 0$) that $\mathrm{d}U = 0$, so $\mathrm{d}Q = -\mathrm{d}W = P\mathrm{d}V$, resulting in
$\Delta S = \int \mathrm{d}S = \int \frac{\mathrm{d}Q}{T} = \int \frac{P\mathrm{d}V}{T} = nR \int \frac{\mathrm{d}V}{V} = nR \ln \frac{V_2}{V_1}$.
Of course, the process is then no longer adiabatic, but still is a suitable reversible alternative between the same begin and end states.

c) $Q = 0$, therefore $\Delta S_{env} = 0$ and we find $\Delta S_{tot} = \Delta S + \Delta S_{env} = \Delta S$. The process proceeds spontaneously if $\Delta S_{tot} > 0$, or if $V_2 > V_1$, as one would expect. If $V_2 < V_1$ (compression), then $\Delta S_{tot} < 0$ and you will have to do work to make the process run.

d) $\Delta S = nR \ln \frac{V_2}{V_1}$. Since the volumes are present as a ratio in the expression, we can stick to the unit (L) and find that $\Delta S = 0.04 \cdot 8.314 \ln \frac{2}{1} = 0.333 \ln 2 = 0.23$ J/K.
For the irreversible process AB it holds that $\mathrm{d}T = 0$, such that for the Helmholtz free energy we find that $\mathrm{d}A \equiv \mathrm{d}U - \mathrm{d}(TS) = \mathrm{d}U - T\mathrm{d}S = 0 - T\mathrm{d}S = -T\mathrm{d}S$, and for the Gibbs free energy $\mathrm{d}G \equiv \mathrm{d}H - \mathrm{d}(TS) = \mathrm{d}H - T\mathrm{d}S = 0 - T\mathrm{d}S = -T\mathrm{d}S$.
At $T = 300$ K we find $\Delta A = \Delta G = -T\Delta S = -300 \cdot 0.23 = -69$ J.

Exercise 8

Assume that $T_1 < T_2$. We denote the final temperature of the entire system as T.
$P_1 = P_2 = P_{ext.} = P$ is constant, so the process is isobaric.
This does require some explanation. Even though the PV-term for liquids and solids hardly changes in processes with pressure changes that are not too large, a spontaneous heat transfer between two liquids can cause a temporary inhomogeneous pressure distribution in the liquids. Therefore it is not straightforward to let such a process proceed strictly isobarically. In case of doubt we can always choose an alternative reversible path, for example by making the thermal contact between the two amounts so bad that the heat transfer is so slow that at every moment during the process the entire system is in thermodynamic equilibrium, and we only have to wait much longer before the temperatures will be equilibrated to T.
In any case, reversible or irreversible, the quantities H and S used below are state functions and thus the change in these quantities is independent of the path.
For an isobaric process the enthalpy H is a suitable function:
$\mathrm{d}H = \mathrm{d}U + P\mathrm{d}V + V\mathrm{d}P = \mathrm{d}U + P\mathrm{d}V = \mathrm{d}Q - P\mathrm{d}V + P\mathrm{d}V = \mathrm{d}Q$.
Since the whole process is running without heat transfer with the surroundings (adiabatic) (of course there is heat transfer between the liquids) it holds that $\mathrm{d}Q = 0$, so $\mathrm{d}H = \mathrm{d}H_1 + \mathrm{d}H_2 = 0$, where H_1 and H_2 are the enthalpies of the two liquids.
According to the definition $C_P = \left(\frac{\partial H}{\partial T}\right)_P$, or $\mathrm{d}H = C_P\mathrm{d}T$ (for C_P we assume that it is independent of the temperature between T_1 and T_2). We have two equal amounts of liquid, so C_P is also equal for both amounts (note: these are not perfect gases so we have no further information on C_P).
The final temperature of both liquids will be equal to T.
The heat transfer will be from 2 to 1 and without loss due to the adiabatic condition, in other words $Q_{2\to1} = -Q_{1\to2}$ and therefore $C_P(T_2 - T) = -C_P(T_1 - T)$, or $2T = T_1 + T_2$, such that $T = \frac{1}{2}(T_1 + T_2)$.
For the change in entropy we find $\mathrm{d}S = \frac{\mathrm{d}Q^{rev}}{T} = \frac{C_P\mathrm{d}T}{T}$. Since S is a state function we can choose an alternative reversible process that results in the same final temperature, as already mentioned above.
$\Delta S = \Delta S_1 + \Delta S_2 = \int_{T_1}^{T} \frac{C_P\mathrm{d}T}{T} + \int_{T_2}^{T} \frac{C_P\mathrm{d}T}{T} = C_P \int_{T_1}^{T} \frac{\mathrm{d}T}{T} + C_P \int_{T_2}^{T} \frac{\mathrm{d}T}{T} = C_P \ln \frac{T}{T_1} + C_P \ln \frac{T}{T_2} = C_P \ln \frac{T^2}{T_1T_2}$.
Filling in the expression found previously for T in terms of T_1 and T_2 results in
$\Delta S = C_P \ln \frac{(T_1+T_2)^2}{4T_1T_2} = C_P \ln \frac{T_1^2+2T_1T_2+T_2^2}{4T_1T_2} = C_P \ln \frac{T_1^2-2T_1T_2+T_2^2+4T_1T_2}{4T_1T_2} = C_P \ln \left(1 + \frac{(T_1-T_2)^2}{4T_1T_2}\right) > 0$,
because $\frac{(T_1-T_2)^2}{4T_1T_2} > 0$.
We had already established that because of the adiabatic process the heat transfer with the surroundings is zero, so $\mathrm{d}S_{env} = \frac{\mathrm{d}Q_{env}}{T} = 0$, with which we find for the total entropy change
$\Delta S_{tot} = \Delta S + \Delta S_{env} = \Delta S > 0$.
This result is in agreement with the entropy change for a spontaneous process according to the second law of thermodynamics.
Moreover, from the expression for ΔS we conclude that (as expected) it is irrelevant whether $T_1 < T_2$ or $T_1 > T_2$.