CORRECTIONS BASED ON AN ANALYTICAL EQUATION OF STATE

Statement

We intend to make use of the following thermodynamic model:

$$v = \frac{RT}{p}\left[1+a+\left(\frac{b}{T}\right)^n\right] \quad \Leftrightarrow \quad Z = 1+a+\left(\frac{b}{T}\right)^n, \quad c_p\left(T,p_0\right) = c+d\left(T-T_0\right)$$

with $a=2.41\cdot10^{-3}$ m³/kg, $b=22.1$ m³/(kg·K), $n=1.6$, $c=638$ J/(kg·K), $d=0.43$ J/(kg·K²), $p_0=100$ kPa and $T_0=298$ K, to model the behaviour of SO_2 in the following problem. Within a vertical cylinder 0.3 m in diameter closed on both sides, a 45 kg piston separates two equal volumes, the upper one filled with air at 105 kPa, and the lower one filled with 0.1 kg of SO_2. Initially, everything is at an ambient temperature of 25 ºC. Thence, the bottom is brought in contact with a heat reservoir at 600 K. Assuming all the other surfaces (including those of the piston) cab be considered adiabatic, find:

a) The initial volume of SO_2.

b) The mass of air trapped.

c) The air temperature at the new equilibrium.

d) The work received by the trapped air.

e) The heat received by the SO_2.

f) The entropy generated in the process.

🇪🇸 Se quiere usar el siguiente modelo termodinámico:

$$v = \frac{RT}{p}\left[1+a+\left(\frac{b}{T}\right)^n\right] \quad \Leftrightarrow \quad Z = 1+a+\left(\frac{b}{T}\right)^n, \quad c_p\left(T,p_0\right) = c+d\left(T-T_0\right)$$

con $a=2.41\cdot10^{-3}$ m³/kg, $b=22.1$ m³/(kg·K), $n=1.6$, $c=638$ J/(kg·K), $d=0.43$ J/(kg·K²), $p_0=100$ kPa y $T_0=298$ K, para modelizar el comportamiento del SO_2 en el siguiente problema. Dentro de un cilindro vertical de 0,3 m de diámetro, un émbolo de 45 kg separa dos volúmenes iguales, el superior contiene aire a 105 kPa, y el inferior 0,1 kg de SO_2. Inicialmente, todo está a 25 ºC. Entonces, se pone en contacto la base inferior con una fuente térmica a 600 K. Suponiendo que todas las demás superficies (incluyendo las del pistón) son adiabáticas, se pide:

a) Volumen de SO_2 inicial.

b) Masa de aire atrapado.

c) Temperatura del aire en el nuevo equilibrio.

d) Trabajo recibido por el aire atrapado.

e) Calor recibido por el SO_2.

f) Generación de entropía en el proceso.

Solution.

a)   The initial volume of SO_2.

From the given equation of state, with $R=R_u/M=8.3/0.064=130$ J/(kg·K), $T=298$ K, $p=p_A+m_Eg/A=105\cdot10^5+45\cdot9.8/0.0707=111\cdot10^5$ Pa (the molar mass of SO_2, $M=0.064$ kg/mol obtained from <u>Gas data tables</u>, and $A=\pi D^2/4=\pi0.3^2/4=70.7\cdot10^{-3}$ m^2):

$$v = \frac{RT}{p}+a+\left(\frac{b}{T}\right)^n = \frac{130\cdot298}{111\cdot10^3}+0.84\cdot10^{-3}+\left(\frac{11.4}{298}\right)^{1.6} = 0.349+0.006 = 0.355 \ \text{m}^3/\text{kg}$$

and thence $V=mv=0.355\cdot0.1=0.0354$ m^3 (35 litres, i.e. the piston is separated 0.0354/0.0707=0.50 m from the base) is the initial volume of SO_2. Notice that the ideal gas model for SO_2 only miss this result by a mere 2%.

b)   The mass of air trapped.

Using the ideal gas model for the air, and knowing that its initial volume coincides with the one just computed, we get:

$$m = \frac{pV}{RT} = \frac{105\cdot10^3\cdot0.0354}{287\cdot298} = 0.0435 \ \text{kg}$$

c)   The air temperature at the new equilibrium.

The trapped air follows an isentropic process because the compression is adiabatic and without dissipation, and thus $T_2/p_2^{(\gamma-1)/\gamma}=T_1/p_1^{(\gamma-1)/\gamma}$, but we do not know the final volume or pressure, although we can establish a system of 3 equations in the 3 unknowns p_{S2}, p_{A2}, T_{A2} (since $T_{S2}=600$ K, and we know $v(T,p)$ in each case):

$$\left.\begin{array}{l} \dfrac{T_{A2}}{T_{A1}}=\left(\dfrac{p_{A2}}{p_{A1}}\right)^{\frac{\gamma-1}{\gamma}} \\[2mm] V_{S2}+V_{A2}=V_{S1}+V_{A1} \\[2mm] p_{S2}=p_{A2}+\dfrac{m_Eg}{A} \end{array}\right\} \Rightarrow \ m_S\left[\frac{R_ST_{S2}}{p_{S2}}\left(1+a+\left(\frac{b}{T_{S2}}\right)^n\right)\right]+m_A\frac{R_AT_{A2}}{p_{A2}}=V_{S1}+V_{A1}$$

which, once numerically solved (e.g. trying in the interval $p_{A1}<p_{A2}<2p_{A1}$), yields $p_{A2}=168$ kPa, and consequently $T_{A2}=298\cdot(167/105)^{0.4/1.4}=340$ K, and the final volume is 25 litres. As for the SO_2, $p_{S2}=p_{A2}+m_Eg/A=167+6=173$ kPa, and $V_{S2}=2\cdot0.0355-0.0255=0.045$ m^3.

d)   The work received by the trapped air.

It is just $W=-\int pdV$ along the isentropic evolution $pV^\gamma=$constant, namely:

$$W_A = -\int pdV \overset{pV^\gamma=\text{const.}}{=} \frac{p_{A1}V_{A1}}{\gamma-1}\left[\left(\frac{V_{A1}}{V_{A2}}\right)^{\gamma-1}-1\right] = \frac{105\cdot10^3\cdot0.0355}{1.4-1}\left[\left(\frac{0.0355}{0.0255}\right)^{1.4-1}-1\right]=1.31 \ \text{kJ}$$

e)   The heat received by the SO_2.

It is the result of the energy balance $\Delta E=Q+W$ for the SO_2, where W is (changed of sign) the sum of the work needed to rise the piston, $m_Eg\Delta z=m_Eg\Delta V/A=45\cdot9.8\cdot(0.0354-0.0255)/0.0707=62$ J, plus the

work needed to compress the air (the 1.31 kJ just computed), i.e. $W=-1.38$ kJ, and the energy change, which, with the perfect gas model would be simply $\Delta E=mc_v\Delta T=0.1\cdot(607-130)\cdot(600-298)=14.4$ kJ (with $c_p=607$ J/(kg·K) from the Gas data tables), must now be computed with the model given in the statement, what is done in terms of enthalpies using $\Delta E=\Delta H-\Delta(pV)=m\Delta h-\Delta(pV)$ and the general expression for enthalpy in terms of T and p, $dh=c_p dT+(1-\alpha T)v dp$, i.e.:

$$\Delta h = \int c_p dT + \int (1-\alpha T)v dp = \int c_p dT + \int \left(v - T \left.\frac{\partial v}{\partial T}\right|_p \right) dp = \int c_p dT + \int \left(a + (1-n)\left(\frac{b}{T}\right)^n \right) dp$$

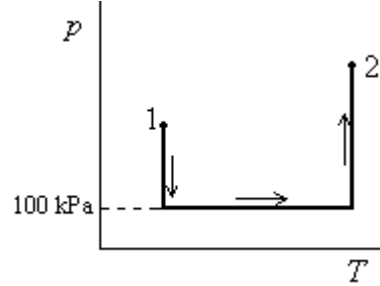where the integration path is sketched in Fig. 1 (to make direct use of the statement data).

Fig. 1. Integration path from state 1 to state 2 through the isobar at p=100 kPa.

Proceeding in that way, with substitution of the model data:

$$h_2 - h_1 = \int_{T_1}^{T_2} c_p (T, p_0) dT + \int_{p_0}^{p_2} \left(v - T_2 \left.\frac{\partial v}{\partial T}\right|_p \right) dp - \int_{p_0}^{p_1} \left(v - T_1 \left.\frac{\partial v}{\partial T}\right|_p \right) dp =$$

$$= c(T_2 - T_1) + \frac{d}{2}\left[(T_2 - T_0)^2 - (T_1 - T_0)^2 \right] + \left[a + (1-n)\left(\frac{b}{T_2}\right)^n \right](p_2 - p_0) - \left[a + (1-n)\left(\frac{b}{T_1}\right)^n \right](p_1 - p_0)$$

one finally gets $\Delta h=212$ kJ, and for the stored energy $\Delta E=m\Delta h-\Delta(pV)= 0.1\cdot212-(173\cdot10^3\cdot0.0455-111\cdot10^3\cdot0.0354)=17.3$ kJ, and finally from the energy balance $Q=\Delta E-W=17.3-(-1.38)=18.7$ kJ.

f)   The entropy generated in the process.

For the combination of all participating subsystems (air A, sulphur dioxide S, and thermal reservoir R), the entropy balance is $S_{gen}=\sum\Delta S=m_A\Delta s_A+m_S\Delta s_S+Q_R/T_R$, where $Q_R=-Q_S=-18.7$ kJ, $\Delta s_A=0$ (the air evolved isentropically), and Δs_S is to be computed using the model given at the statement, by means of the general entropy expression in terms of T and p, $ds=(c_p/T)dT-\alpha v dp$, i.e.:

$$\Delta s = \int \frac{c_p}{T} dT - \int \alpha v dp = \int \frac{c_p}{T} dT - \int \left.\frac{\partial v}{\partial T}\right|_p dp = \int \frac{c+d(T-T_0)}{T} dT - \int \left[\frac{R}{p}\left(1 - \frac{n}{T}\left(\frac{b}{T}\right)^n \right) \right] dp$$

where the integration path sketched in Fig. 1 must be followed again. Substituting the data yields $\Delta s_S=540$ J/(kg·K), and finally $S_{gen}=\sum\Delta S=m_S\Delta s_S+Q_R/T_R=54+(-31)=23$ J/K. In this case, the perfect gas model would give a much lower value, $S_{gen\_PGM}=5$ J/K.

Comments. As a general remark, one might conclude that the extra effort demanded by non-simple models for substances, may not be justified by the minor improvement in accuracy, when the computations are manually done. But, on one side, departure from the perfect gas model may be much larger at greater pressure, and, on the other hand, the intention was to show the general procedure with a manageable exercise.