CORRESPONDING STATES CORRECTIONS

Statement

A horizontal cylinder-piston device holds 1 m^3 of carbon dioxide at 260 K and 100 kPa, surrounded by an ambient at 288 K and 100 kPa. Besides this state (initial state or state 1) two other states are to be considered: the state of thermomechanical equilibrium with the environment (dead state or state 0) and the state of saturated vapour at 260 K (state 2). Use a constant-value c_p=800 J.kg^{-1}.K^{-1} for the gas at low pressure, and both, the ideal gas model and the corresponding state model to find:

a) Mass of gas inside.

b) Heat received from thermal contact at constant pressure.

c) Maximum work obtainable from the above relaxation process.

d) Vapour pressure at 260 K.

e) Volume at the saturated vapour state.

f) Change in internal energy, enthalpy and entropy between states 1 and 2.

g) Work spent (from a mechanical reservoir) assuming an isothermal compression from 1 to 2.

h) Minimum work required to go from state 1 to state 2 (and comparison with the above result).

i) General expression of the Joule-Thomson coefficient as a function of the compressibility coefficient, and its value at state 2.

j) Make a sketch in the p-v diagram (really p_R-v_R) of the isotherm T=260 K, and, in another diagram of the chemical potential (better $\mu/(RT)$) as a function of lnp_R for T=260 K.

🔴 En un dispositivo cilindro-émbolo horizontal se tiene 1 m^3 de dióxido de carbono a 260 K y 100 kPa, estando la atmósfera exterior a 288 K y 100 kPa. Además de este estado (inicial o estado 1) se van a considerar otros dos: el estado de equilibrio termomecánico con la atmósfera (estado muerto o estado 0) y el estado en que empieza la transición gas-líquido a 260 K (estado saturado o estado 2). Tómese un valor constante c_p=800 J.kg^{-1}.K^{-1} para el gas a bajas presiones, y calcúlese con el modelo de gas ideal y el de estados correspondientes:

a) Masa de gas encerrado.

b) Calor que recibiría la masa de gas si se atemperase a presión constante.

c) Trabajo límite que podría extraerse en el proceso de atemperamiento a p constante.

d) Presión en el estado de gas saturado (presión de vapor a 260 K).

e) Volumen del gas en el punto de vapor saturado.

f) Variación de energía interna, entalpía y entropía entre los estados 1 y 2.

g) Trabajo aportado (desde un depósito mecánico reversible) suponiendo una compresión isoterma de 1 a 2.

h) Trabajo mínimo necesario para pasar del estado 1 al estado 2 (y criticar la diferencia con el del apartado anterior).

i) Expresión general del coeficiente de Joule-Thomson en función del coeficiente de compresibilidad, y valor en el estado 2.

j) Representar esquemáticamente en un diagrama p-v (en realidad p_R-v_R) la isoterma $T=260$ K, y en otro diagrama el potencial químico, en realidad $\mu/(RT)$, en función de $\ln p_R$ para $T=260$ K, para los tres casos siguientes: 1) para el modelo de gas ideal (completado con el de líquido incompresible a partir del punto bifásico), 2) para el modelo de estados correspondientes, 3) para el modelo de van der Waals reducido, dando en este último caso las expresiones explícitas $\mu(v_R)$ y $p_R(v_R)$.

Solution. We use the perfect gas model (PGM), or the corresponding state model (CSM) when needed, with constant thermal capacity in both cases (in the ideal gas limit ($p \to 0$) c_p varies almost linearly (e.g. $c_p=753$ J/(kg·K) at the triple-point temperature, $T_{tr}=216$ K, and $c_p=850$ J/(kg·K) at the triple-point temperature, $T_{cr}=304$ K). Figure 1 is a sketch in the Z-p diagram of the three states mentioned.
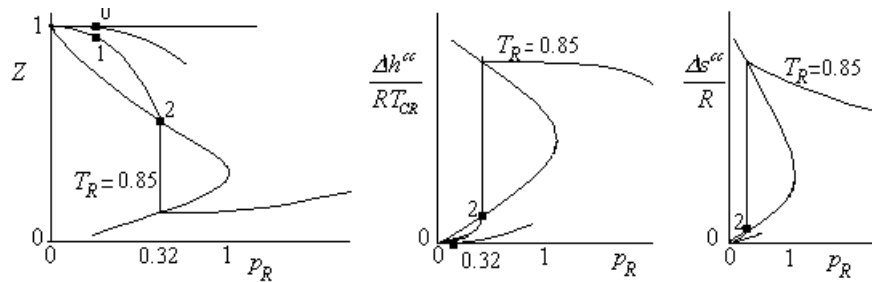

Fig. 1. State points in the corresponding states diagrams.

a) Mass of gas inside.

With the PGM, $m=pV/(RT)=10^5 \cdot 1/(189 \cdot 260)=2.04$ kg, with $R_{CO2}=(8.3/0.044=189$ J/(kg·K). With the CSM:

$$m = \frac{pV}{ZRT} = \frac{10^5 \cdot 1}{0.99 \cdot 189 \cdot 260} = 2.06 \text{ kg}$$

where the compressibility factor Z has been obtained from the corresponding state diagram, at state 1, $Z(p_{R1},T_{R1})=Z(0.1/7.4;260/304)=Z(0.01;0.85)=0.99$. In this state, the density correction by non-ideality (compressibility correction) is very small, always increasing the ideal-gas value (for temperatures below Boyle's temperature, $T_{Boyle} \approx 2.5 T_{cr}$).

b) Heat received from thermal contact at constant pressure.

$Q=\Delta H=m(\Delta h^{id}-\Delta h_0^{cc}+\Delta h_1^{cc}) \approx m\Delta h^{id}=mc_p(T_0-T_1)=2.06 \cdot 800(288-260)=46$ kJ, since enthalpy corrections for compressibility were very small. It may be compared with the best value available (NIST) $Q=m(h_0-h_1)=47.6$ kJ.

c) Maximum work obtainable from the above relaxation process.

$W_{min}=\Delta\Phi=\Delta(U+p_0V-T_0S)=35+10-49=-4$ kJ (i.e. up to 4 kJ of work could have been obtained), since energy corrections ($U=H-pV$, $\Delta U=\Delta H+(Z-1)RT$) and entropy corrections were very small, and $\Delta U=mc_v(T_0-T_1)=2.06 \cdot (800-8.3/0.044) \cdot (288-260)=35$ kJ, $p_0\Delta V=mR\Delta T=2.06 \cdot 189 \cdot (288-260) =10$ kJ, and $\Delta S=mc_p\ln(T_0/T_1)-mR\ln(p_0/p_1) =2.06 \cdot 800 \cdot \ln(288/260)-0=169$ J/K.

d) Vapour pressure at 260 K.

The ideal gas model cannot condense, and thence there is no relation to equilibrium vapour pressure. From the corresponding states diagram Z-p_R, the liquid-vapour-equilibrium at $T_R=0.85$ is $p_{R,vap}=0.32$, thus $p_{v2}=2.36$ MPa (the more-accurate Antoine's correlation gives 2.42 MPa). It may be compared with the best value available (NIST) $p_{v2}=2.416$ MPa.

e) Volume at the saturated vapour state.

With the ideal gas model, $V_2=mRT/p=2.04 \cdot 189 \cdot 260/(2.42 \cdot 10^6)=0.042$ m^3, although it is more accurate to directly compute V_2 from Boyle's law: at constant temperature, $V_2=V_1 p_1/p_2=1 \cdot 10^5/(2.42.10^6)=0.041$ m^3.

With the corresponding states model:

$$V = \frac{ZmRT}{p} = \frac{0.77 \cdot 2.06 \cdot 189 \cdot 260}{2.36 \cdot 10^6} = 0.032 \text{ m}^3$$

where the compressibility factor Z has been obtained from the corresponding state diagram: $Z(p_{R2},T_{R2})=Z(2.36/7.4;260/304)=Z(0.33;0.85)=0.77$.

f) Change in internal energy, enthalpy and entropy between states 1 and 2.

As usual, we compute energy changes in terms of enthalpy changes, because only enthalpy data are usually available. $\Delta U=\Delta H-(p_2 V_2-p_1 V_1)$, $\Delta H=m(\Delta h^{\text{id}}-\Delta h_2^{\text{cc}}+\Delta h_1^{\text{cc}})$, $\Delta S=m(\Delta s^{\text{id}}-\Delta s_2^{\text{cc}}+\Delta s_1^{\text{cc}})$. With the corresponding-state-correction diagram for enthalpy (see Thermal Data) one finds $\Delta h_2^{\text{cc}}/(RT_{\text{cr}})=0.6$ (or $\Delta h_2^{\text{cc}}/T_{\text{cr}}=5$ J/(mol·K)), and similarly $\Delta s_2^{\text{cc}}/R=0.6$ (or $\Delta s_2^{\text{cc}}=5$ J/(mol·K)), thence $\Delta h_2^{\text{cc}}=5 \cdot 304/0.044=35$ kJ/kg and $\Delta s_2^{\text{cc}}=110$ J/kg. Corrections at state 1 are negligible, thus we have $\Delta H=m(c_p \Delta T-\Delta h_2^{\text{cc}}+\Delta h_1^{\text{cc}})=2.06 \cdot (0-35+0)=-72$ kJ, $\Delta S=m(c_p \ln(T_2/T_1)-R\ln(p_2/p_1) \quad -\Delta s_2^{\text{cc}}+\Delta s_1^{\text{cc}})$ $=2.06 \cdot (0-(8.3/0.044) \cdot \ln(2.36/0.1)-110+0)=-1.5$ kJ/K, and $\Delta U=\Delta H-(p_2 V_2-p_1 V_1)=$ $=-72-(2360 \cdot 0.032-100 \cdot 1)=-48$ kJ. These values may be compared with the best value available (NIST): $\Delta H=-78.9$ kJ, $\Delta S=-1.46$ kJ/K, and $\Delta U=-56$ kJ.

g) Work spent (from a mechanical reservoir) assuming an isothermal compression from 1 to 2.

With the CSM, $W_{u12}=W_{12}+p_0(V_2-V_1)=E_2-E_1-Q_{12}+p_0(V_2-V_1)=E_2-E_1-T_2(S_2-S_1)+p_0(V_2-V_1)=200$ kJ (with the PGM $W_{u12}=220$ kJ).

h) Minimum work required to go from state 1 to state 2 (and comparison with the above result).

$W_{u12min}=E_2-E_1+p_0(V_2-V_1)-T_0(S_2-S_1)=240$ kJ by the CSM.

Question. How can the minimum be larger than the actual? The answer lies in the fact that, for the actual work, we have used a second heat source (at 260 K) that brings in extra exergy.

i) General expression of the Joule-Thomson coefficient as a function of the compressibility coefficient, and its value at state 2.

From the definition of Joule-Thomson or Joule-Kelvin coefficient, μ_{JK}:

$$\mu_{\text{JK}} \equiv \left.\frac{\partial T}{\partial p}\right|_h = \frac{-(1-\alpha T)v}{c_p}, \text{ with } v=\frac{ZRT}{p} \text{ and } \alpha=\frac{1}{Z}\left.\frac{\partial Z}{\partial T}\right|_p + \frac{1}{T}, \text{ i.e. } \mu_{\text{JK}} \equiv \left.\frac{\partial T}{\partial p}\right|_h = \frac{RT^2}{c_p p}\left.\frac{\partial Z}{\partial T}\right|_p$$

From the corresponding states diagram we can graphically evaluate $\left.\frac{\partial Z}{\partial T}\right|_p=2.6$ K^{-1}, and thence μ_{JK} $_2=0.021$ K/Pa. Of course, with the PGM $\mu_{\text{JK}}=0$, since $\alpha=1/T$.

j) Make a sketch in the p-v diagram (really p_R-v_R) of the isotherm $T=260$ K, and, in another diagram, of the chemical potential μ, or better $\mu/(RT)$ to be dimensionless, as a function of $\ln p_R$ for $T=260$ K (recall that for pure substances the chemical potential coincides with Gibbs potential $g(T,p)$).

Instead of the CSM we use the PGM and the reduced van-der-Waals's model (vWRM),
$p_R = \dfrac{8T_R}{3v_R - 1} - \dfrac{3}{v_R^2}$, to work analytically (instead of graphically). The PGM with v_{cr} based on vWM,

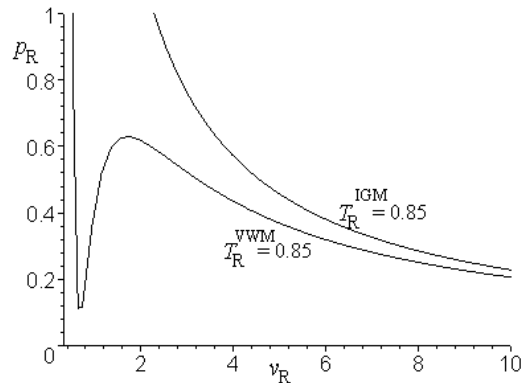reduces to $p_R = \dfrac{8T_R}{3v_R}$, what yields the plot:

Fig. 2. The reduced isotherm $T=260$ K ($T_R=0.85$) in the reduced p-v diagram, for both the ideal gas model and for the reduced van der Waals model.

The chemical potential μ, must be obtained from $d\mu = -sdT + vdp \rightarrow d\mu = vdp$ along an isotherm, and

we want to plot $\dfrac{\mu(T,p)}{RT} = \dfrac{\mu(T,p \rightarrow 0)}{RT} + \displaystyle\int\limits_{p \rightarrow 0}^{p} \dfrac{vdp}{RT}$, not an easy task since we do not have $v(p)$ but

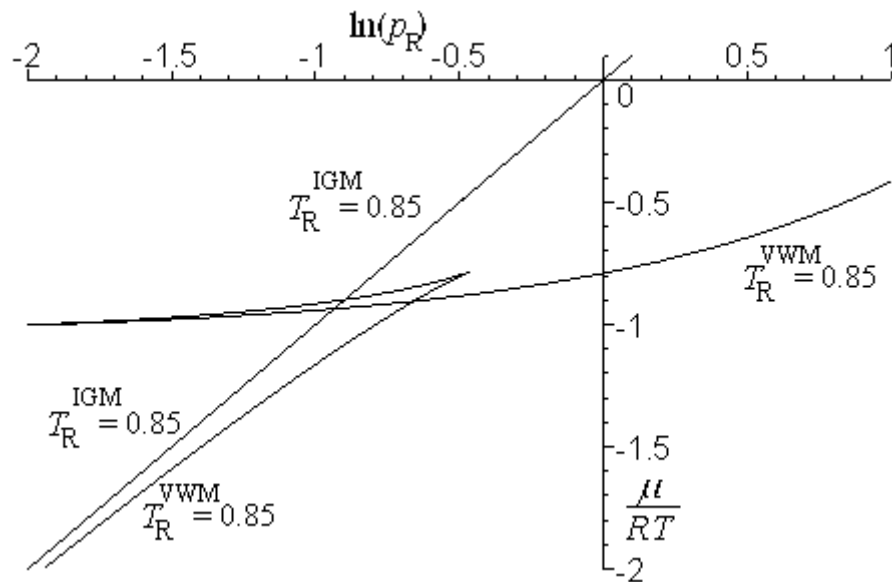$p(v)$; proceeding in parametrics, i.e. computing $\mu(v)$ and $p(v)$, one finally gets (details aside):

Fig. 3. The reduced isotherm $T=260$ K ($T_R=0.85$) in the reduced $\mu/(RT)$-$\ln p$ diagram, for the ideal gas model (PGM) and for the reduced van der Waals model (VWM).

Comments. The vapour pressure at this temperature may be found by Maxwell's rule (it coincides with the crossing point in the $\mu/(RT)$-$\ln p$ diagrams).

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