COMPATIBILITY OF EQUATIONS OF STATE

Statement

Thermodynamic behaviour of a gas is to be modelled by the equations of state: $v(T,p)=a_1+a_2T+a_3/T+a_4T/p+a_5p/T$ and $u(T,p)=b_1+b_2T+b_3/T+b_4T/p+b_5p/T$, where $a_1...b_5$ are experimental constants. One wants:

a) Deduce the relations amongst the coefficients to have a compatible model (take into account also that for $p\to0$ the ideal gas model must be recovered).

b) Compute c_p, α, κ, Z, Δh and Δs for the model given in the case of the odd coefficients being zero.

Se pretende describir el comportamiento termodinámico de cierto gas mediante las ecuaciones de estado $v(T,p)=a_1+a_2T+a_3/T+a_4T/p+a_5p/T$ y $u(T,p)=b_1+b_2T+b_3/T+b_4T/p+b_5p/T$, siendo $a_1...b_5$ constantes a determinar experimentalmente. Se pide:

a) Determinar para qué valores de las constantes puede ser válido el modelo (téngase en cuenta que para $p\to0$ se debe recuperar el modelo de gas ideal).

b) Calcular c_p, α, κ, Z, Δh y Δs para el modelo dado suponiendo que los coeficientes impares del desarrollo dado son nulos.

Solution

a) Deduce the relations amongst the coefficients to have a compatible model (take into account also that for $p\to0$ the ideal gas model must be recovered).

Maxwell equation must be verified, thus:

$$\left.\frac{\partial v}{\partial T}\right|_p=\left.\frac{\partial(-s)}{\partial p}\right|_T=\left.\frac{-\dfrac{\partial u+p\partial v}{T}}{\partial p}\right|_T\Rightarrow a_2-\frac{a_3}{T^2}+\frac{a_4}{p}-\frac{a_5p}{T^2}=\frac{-1}{T}\left(\frac{-b_4T}{p^2}-\frac{b_5}{T}\right)-\frac{p}{T}\left(\frac{a_4T}{p^2}+\frac{a_5}{T}\right)$$

what implies that the coefficients must verify: $a_2=0$, $b_4=0$ and $b_5=a_3$. Besides, if the ideal-gas behaviour is to be approached at $p\to0$, $a_4=R$. In summary:

$$v=a_1+\frac{a_3}{T}+\frac{RT}{p}+\frac{a_5p}{T}\quad\text{and}\quad u=b_1+b_2T+\frac{b_3}{T}+\frac{a_3p}{T}$$

b) Compute c_p, α, κ, Z, Δh and Δs for the model given in the case of the odd coefficients being zero.

From the definition of the functions (4.9-11) and (4.15), and without odd coefficients:

$$c_p\equiv T\left.\frac{\partial s}{\partial T}\right|_{p,n_i}=\left.\frac{\partial u+p\partial v}{\partial T}\right|_{p,n_i}=\left(b_2-\frac{b_3}{T^2}+\frac{b_4}{p}-\frac{b_5p}{T^2}\right)+p\left(a_2-\frac{a_3}{T^2}+\frac{a_4}{p}-\frac{a_5p}{T^2}\right)=$$

$$=b_2-\frac{b_3}{T^2}-\frac{2b_5p}{T^2}+R-\frac{a_5p^2}{T^2}=b_2+R$$

$$\alpha\equiv\frac{1}{V}\left.\frac{\partial V}{\partial T}\right|_{p,n_i}=\frac{a_2-\dfrac{a_3}{T^2}+\dfrac{a_4}{p}-\dfrac{a_5p}{T^2}}{v(T,p)}=\frac{-b_5p+RT^2-a_5p^2}{T\left(a_1Tp+b_5p+RT^2+a_5p^2\right)}=\frac{1}{T}$$

$$\kappa \equiv \frac{-1}{V}\frac{\partial V}{\partial p}\bigg|_{T,n_i} = \frac{-\left(\frac{a_4 T}{p^2}+\frac{a_5}{T}\right)}{v(T,p)} = \frac{RT^2 - a_5 p^2}{p\left(a_1 Tp + b_5 p + RT^2 + a_5 p^2\right)} = \frac{1}{p}$$

$$Z \equiv \frac{pv}{RT} = \frac{p\left(a_1 Tp + b_5 p + RT^2 + a_5 p^2\right)}{RT} = 1 + \left(\frac{a_1}{RT}+\frac{a_3}{RT^2}\right)p + \left(\frac{a_5}{RT^2}\right)p^2 = 1$$

From the general expressions (4.17-18):

$$dh = c_p dT + (1-\alpha T)vdp = \left(b_2 + R\right)dT + (1-\frac{1}{T}T)vdp \rightarrow h_2 - h_1 = \left(b_2 + R\right)\left(T_2 - T_1\right)$$

$$ds = \frac{c_p}{T}dT - \alpha vdp = \frac{b_2 + R}{T}dT - \frac{1}{T}\frac{RT}{p}dp \rightarrow s_2 - s_1 = \left(b_2 + R\right)\ln\frac{T_2}{T_1} - R\ln\frac{p_2}{p_1}$$

Comments. The idea was to notice that thermodynamic data might be redundant and/or conflicting, and that many thermodynamic functions are related among themselves and can be deduced from others.

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