Atividade Somativa Semana 9

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Problem 5.14. The partial-derivative relations derived in Problems 1.46, 3.33, and 5.12, plus a bit more partial-derivative trickery, can be used to derive a completely general relation between C_P and C_V.

(a) With the heat capacity expressions from Problem 3.33 in mind, first consider S to be a function of T and V. Expand dS in terms of the partial derivatives $(\partial S/\partial T)_V$ and $(\partial S/\partial V)_T$. Note that one of these derivatives is related to C_V.

(b) To bring in C_P, consider V to be a function of T and P and expand dV in terms of partial derivatives in a similar way. Plug this expression for dV into the result of part (a), then set $dP = 0$ and note that you have derived a nontrivial expression for $(\partial S/\partial T)_P$. This derivative is related to C_P, so you now have a formula for the difference $C_P - C_V$.

(c) Write the remaining partial derivatives in terms of measurable quantities using a Maxwell relation and the result of Problem 1.46. Your final result should be

$$C_P = C_V + \frac{TV\beta^2}{\kappa_T}.$$

(d) Check that this formula gives the correct value of $C_P - C_V$ for an ideal gas.

(e) Use this formula to argue that C_P cannot be less than C_V.

(f) Use the data in Problem 1.46 to evaluate $C_P - C_V$ for water and for mercury at room temperature. By what percentage do the two heat capacities differ?

(g) Figure 1.14 shows measured values of C_P for three elemental solids, compared to predicted values of C_V. It turns out that a graph of β vs. T for a solid has same general appearance as a graph of heat capacity. Use this fact to explain why C_P and C_V agree at low temperatures but diverge in the way they do at higher temperatures.

a)

Sabendo que

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \qquad C_P = \left(\frac{\partial H}{\partial T}\right)_P$$

Escrevendo dS sabendo que S é função de T e V

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \quad (1)$$

Reescrevendo as expressões de C_v e C_p levando as identidades Termodinâmicas,

$$dU = TdS - PdV + \mu dN$$

$$dH = TdS + VdP + \mu dN$$

$$C_v = T\left(\frac{\partial S}{\partial T}\right)_V + \mu\left(\frac{\partial N}{\partial T}\right)_V$$

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_P + \mu\left(\frac{\partial N}{\partial T}\right)_P$$

Retirando a contribuição do potencial químico,

$$\frac{C_v}{T} = \left(\frac{\partial S}{\partial T}\right)_V$$

Que é o 1º termo de dS.

b)

Sabendo que $V = V(T, P)$

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP$$

Tomando $dP = 0$

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT$$

Substituindo em (1) escrevemos

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P dT$$

Escrevemos

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

$$\frac{C_p}{T} \qquad \frac{C_v}{T}$$

$$C_p - C_v = T\left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p \quad (2)$$

c) Como

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

Pelas Relações de Maxwell. Escrevemos (2)

$$C_p - C_v = T\left(\frac{\partial p}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_p$$

Sabendo que também

$$C_p - C_v = -T\left(\frac{\partial V}{\partial T}\right)_p^2 \Big/ \left(\frac{\partial V}{\partial p}\right)_T$$

Como

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \; ; \; k_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$$

Escrevemos $C_p - C_v$ como

$$C_p - C_v = -T(\beta V)^2 / (-k_T T)$$

$$C_p - C_V = \frac{TV\beta^2}{\kappa_T} \quad (3)$$

d) Para um gás ideal

$$\beta = \frac{1}{T} \; ; \; \kappa_T = \frac{1}{P}$$

O que faz (3)

$$C_p - C_V = \frac{TV/T^2}{1/P} = \frac{PV}{T} = Nk_B$$

e) C_p não pode ser menor já que

$$C_p = C_V + Nk_B$$

Sendo que $Nk_B > 0$.

f) Usando os dados do problema (1.46) encontramos

$$C_p - C_v = \frac{298 \cdot 10^{-6} (2{,}57 \times 10^{-4})^2}{4{,}52 \times 10^{-10}}$$

$$= 0{,}0435 \, J/K$$