Termodinámica

Corrección de la Tarea 9

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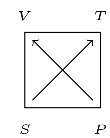
Problema 1

Antes de reducir derivadas, calculemos las que nos serán útiles usando tan sólo el cuadrado termodinámico. Recordemos que



$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P; \quad K_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T; \quad C_V = T\left(\frac{\partial S}{\partial T}\right)_V; \quad C_P = C_V + \frac{TV\alpha^2}{K_T}.$$

Primera relación:

$$\begin{aligned}\left(\frac{\partial P}{\partial T}\right)_V &= -\left(\frac{\partial P}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P \\ &= \frac{1}{K_T V}\alpha V \\ &= \frac{\alpha}{K_T},\end{aligned}$$

por lo tanto

$$\boxed{\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T = \frac{\alpha}{K_T}\ .} \tag{1.1}$$

Segunda relación:

$$\begin{aligned}\left(\frac{\partial P}{\partial S}\right)_T &= -\left(\frac{\partial T}{\partial V}\right)_P \\ &= -\frac{1}{\alpha V},\end{aligned}$$

por lo tanto

$$\boxed{\left(\frac{\partial P}{\partial S}\right)_T = -\frac{1}{\alpha V}\ .} \tag{1.2}$$

Tercera relación:

$$\begin{aligned}\left(\frac{\partial V}{\partial T}\right)_S &= -\left(\frac{\partial V}{\partial S}\right)_T\left(\frac{\partial S}{\partial T}\right)_V \\ &= -\left(\frac{\partial T}{\partial P}\right)_V\frac{C_V}{T} \\ &= \left(\frac{\partial T}{\partial V}\right)_P\left(\frac{\partial V}{\partial P}\right)_T\frac{C_V}{T} \\ &= \frac{1}{\alpha V}(-K_T V)\frac{C_V}{T},\end{aligned}$$

por lo tanto

$$\boxed{\left(\frac{\partial V}{\partial T}\right)_S = -\frac{K_T C_V}{\alpha T}\ .} \tag{1.3}$$

Cuarta relación:

$$\begin{aligned}\left(\frac{\partial T}{\partial P}\right)_S &= -\left(\frac{\partial T}{\partial S}\right)_P\left(\frac{\partial S}{\partial P}\right)_T \\ &= \frac{T}{C_P}\left(\frac{\partial V}{\partial T}\right)_P,\end{aligned}$$

por lo tanto

$$\boxed{\left(\frac{\partial T}{\partial P}\right)_S = \frac{T\alpha V}{C_P}\ .} \tag{1.4}$$

Quinta relación:

$$\begin{aligned}\left(\frac{\partial V}{\partial S}\right)_P &= \left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial T}{\partial V}\right)_P \\ &= \frac{\alpha V T}{C_P},\end{aligned}$$

por lo tanto

$$\boxed{\left(\frac{\partial V}{\partial S}\right)_P = \frac{\alpha V T}{C_P}\ .} \tag{1.5}$$

Sexta relación:

$$\begin{aligned}\left(\frac{\partial V}{\partial P}\right)_S &= \left(\frac{\partial V}{\partial T}\right)_S\left(\frac{\partial T}{\partial P}\right)_S \\ &= -\frac{k_T C_V}{\alpha T}\frac{T\alpha V}{C_P},\end{aligned}$$

por lo tanto

$$\boxed{\left(\frac{\partial V}{\partial P}\right)_S = -\frac{C_V}{C_P}K_T V\ .} \tag{1.6}$$

a) La primera derivada que queremos reducir es $\left(\frac{\partial S}{\partial V}\right)_H$. Recordemos que $dH = T\,dS + V\,dP$, luego

$$\begin{aligned}
\left(\frac{\partial S}{\partial V}\right)_H &= -\left(\frac{\partial S}{\partial H}\right)_V \left(\frac{\partial H}{\partial V}\right)_S \\
&= -\left[\left(\frac{\partial H}{\partial S}\right)_V\right]^{-1} \left(\frac{\partial H}{\partial V}\right)_S \\
&= -\left[T + V\left(\frac{\partial P}{\partial S}\right)_V\right]^{-1} \left[V\left(\frac{\partial P}{\partial V}\right)_S\right] \\
&= \left[T - V\left(\frac{\partial T}{\partial V}\right)_S\right]^{-1} \left[V\left(\frac{\partial P}{\partial S}\right)_V \left(\frac{\partial S}{\partial V}\right)_P\right] \\
&= \left[T + V\left(\frac{\partial T}{\partial S}\right)_V \left(\frac{\partial S}{\partial V}\right)_T\right] \left[-V\left(\frac{\partial T}{\partial V}\right)_S \left(\frac{\partial P}{\partial T}\right)_S\right] \\
&= \left[T + V\frac{T}{C_V}\left(\frac{\partial P}{\partial T}\right)_V\right] \left[-V\left(\frac{\partial T}{\partial S}\right)_V \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial P}{\partial S}\right)_T \left(\frac{\partial S}{\partial T}\right)_P\right] \\
&= \left[T + \frac{TV\alpha}{C_V K_T}\right]^{-1} \left[-V\frac{T}{C_V}\frac{\alpha}{K_T}\left(-\frac{1}{\alpha V}\right)\frac{C_P}{T}\right] \\
&= \frac{\frac{C_P}{C_V K_T}}{T + \frac{TV\alpha}{C_V K_T}},
\end{aligned}$$

por lo tanto

$$\boxed{\left(\frac{\partial S}{\partial V}\right)_H = \frac{C_P}{TC_V K_T + TV\alpha}\ .} \tag{1.7}$$

b) La siguiente derivada a reducir es $\left(\frac{\partial H}{\partial G}\right)_F$. Recordemos que $dG = -S\,dT + V\,dP$ y $dF = -S\,dT - P\,dV$.

$$\begin{aligned}
\left(\frac{\partial H}{\partial G}\right)_F &= T\left(\frac{\partial S}{\partial G}\right)_F + V\left(\frac{\partial P}{\partial G}\right)_F \\
&= T\left[\left(\frac{\partial G}{\partial S}\right)_F\right]^{-1} + V\left[\left(\frac{\partial G}{\partial P}\right)_F\right]^{-1} \\
&= T\left[-S\left(\frac{\partial T}{\partial S}\right)_F + V\left(\frac{\partial P}{\partial S}\right)_F\right] + V\left[-S\left(\frac{\partial T}{\partial P}\right)_F + V\right]^{-1} \\
&= T\left[S\left(\frac{\partial T}{\partial F}\right)_S \left(\frac{\partial F}{\partial S}\right)_T - V\left(\frac{\partial P}{\partial F}\right)_S \left(\frac{\partial F}{\partial S}\right)_P\right]^{-1} + V\left[S\left(\frac{\partial T}{\partial F}\right)_P \left(\frac{\partial F}{\partial P}\right)_T + V\right]^{-1} \\
&= T\left[S\left(-S - P\left(\frac{\partial V}{\partial T}\right)_S\right)^{-1}\left(-P\left(\frac{\partial V}{\partial S}\right)_T\right)\right. \\
&\left. -V\left(-S\left(\frac{\partial T}{\partial P}\right)_S - P\left(\frac{\partial V}{\partial P}\right)_S\right)^{-1}\left(-S\left(\frac{\partial T}{\partial S}\right)_P - P\left(\frac{\partial V}{\partial S}\right)_P\right)\right]^{-1} \\
&+ V\left[S\left(-S - P\left(\frac{\partial V}{\partial T}\right)_P\right)^{-1}\left(-P\left(\frac{\partial V}{\partial T}\right)_P\right) + V\right]^{-1} \\
&= T\left[S\left(-S + \frac{PK_T C_V}{\alpha T}\right)^{-1}\left(-\frac{PK_T}{\alpha}\right)\right. \\
&\left. +V\left(\frac{ST\alpha V}{C_P} - \frac{PVK_T C_V}{C_P}\right)^{-1}\left(-\frac{ST}{C_P} - \frac{P\alpha VT}{C_P}\right)\right]^{-1}.
\end{aligned}$$

$$\therefore \left(\frac{\partial H}{\partial G}\right)_F = T\left[S\left(\frac{ST\alpha - PK_TC_V}{\alpha V}\right)^{-1}\left(\frac{PK_T}{\alpha}\right) - V\left(\frac{ST\alpha V - PVK_TC_V}{C_P}\right)^{-1}\left(\frac{ST + PVT\alpha}{C_P}\right)\right]^{-1}$$
$$+ V\left[-S(S + PV\alpha)^{-1}(PK_TV) + V\right]^{-1}$$
$$= T\left[\frac{SPK_T}{ST\alpha - PK_TC_V} - \frac{ST + PVT\alpha}{ST\alpha - K_TC_V}\right]^{-1} + V\left[V - \frac{SPK_TV}{S + PV\alpha}\right]^{-1}$$
$$= T\left[\frac{SPTK_T - ST - PVT\alpha}{ST\alpha - PK_TC_V}\right]^{-1} + V\left[\frac{SV + PV^2\alpha - SPVK_T}{S + PV\alpha}\right]^{-1}$$
$$= \frac{ST\alpha - PK_TC_V}{SPK_T - s - PV\alpha} + \frac{S + PV\alpha}{S + PV\alpha - SPK_T}$$
$$= \frac{ST\alpha - PK_TC_V - S - PV\alpha}{SPK_T - S - PV\alpha}.$$

Luego

$$\boxed{\left(\frac{\partial H}{\partial G}\right)_F = 1 + \frac{ST\alpha - PK_TC_V - SPK_T}{SPK_T - S - PV\alpha}\ .} \tag{1.8}$$

c) Finalmente, reduzcamos la derivada $\left(\frac{\partial F}{\partial \mu}\right)_S$. Así como una vez necesitamos el diferencial del potencial de Gobbs, del potencial Entalpía y el potencial de Helmholtz, ahora necesitaremos el difirencial del potencial electroquímico. Recordemos que, según la relación de Euler,

$$U = TS - PV + \mu N,$$

por lo que

$$dU = T\,dS + S\,dT - P\,dV - V\,dP + \mu\,dN + N\,d\mu;$$

pero $dU = T\,dS - P\,dV + \mu\,dN$, luego

$$0 = S\,dT - V\,dP + N\,d\mu.$$

De aqui concluímos que

$$d\mu = -\frac{S}{N}\,dT + \frac{V}{N}\,dP.$$

De esta forma, tendremos

$$
\begin{aligned}
\left(\frac{\partial F}{\partial \mu}\right)_S &= -S\left(\frac{\partial T}{\partial \mu}\right)_S - P\left(\frac{\partial V}{\partial \mu}\right)_S \\
&= -S\left[\left(\frac{\partial \mu}{\partial T}\right)_S\right]^{-1} - P\left[\left(\frac{\partial \mu}{\partial V}\right)_S\right]^{-1} \\
&= -S\left[-\frac{S}{N} + \frac{V}{N}\left(\frac{\partial P}{\partial T}\right)_S\right]^{-1} - P\left[-\frac{S}{N}\left(\frac{\partial T}{\partial V}\right)_S + \frac{V}{N}\left(\frac{\partial P}{\partial V}\right)_S\right]^{-1} \\
&= S\left[\frac{S}{N} - \frac{V}{N}\frac{C_P}{T\alpha V}\right]^{-1} + P\left[\frac{S}{N}\left(-\frac{\alpha T}{K_T C_V}\right) - \frac{V}{N}\left(-\frac{C_P}{C_V K_T V}\right)\right]^{-1} \\
&= S\left[\frac{S}{N} - \frac{C_P}{NT\alpha}\right]^{-1} + P\left[-\frac{ST\alpha}{NK_T C_V} + \frac{C_P}{NK_T C_V}\right]^{-1} \\
&= S\frac{NT\alpha}{ST\alpha - C_P} + P\frac{NK_T C_V}{C_P - ST\alpha} \\
&= \frac{SNT\alpha - PNK_T C_V}{ST\alpha - C_P}.
\end{aligned}
$$

Por lo tanto

$$
\boxed{\left(\frac{\partial F}{\partial \mu}\right)_S = \frac{SNT\alpha - PNK_T C_V}{ST\alpha - C_P}\ .} \tag{1.9}
$$

Problema 2

De la ecuación (1.6) concluímos inmediatamente que

$$
\begin{aligned}
K_S \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S \\
&= -\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_S\left(\frac{\partial T}{\partial P}\right)_S \\
&= \frac{1}{V}\left(\frac{K_T C_V}{\alpha T}\right)\frac{T\alpha V}{C_P} \\
&= \frac{C_V}{C_P}K_T.
\end{aligned}
$$

Por lo tanto, el coeficiente de expansión isotérmica se relaciona con el coeficiente de expansión isentrípica (o adiabática) mediante la relación

$$
K_S = \frac{C_V}{C_P}K_T.
$$

Problema 3

Queremos calcular $C_v(T, P)$ sabiendo que

$$
H = AS^2N^{-1}\ln\left(\frac{P}{P_o}\right).
$$

Sabemos que

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

Luego

$$\begin{aligned}
V &= \frac{\partial H}{\partial P} \\
\Rightarrow \quad V &= \frac{AS^2}{N}\frac{1}{P} \\
\Rightarrow \quad PV &= \frac{AS^2}{N}. \\
\therefore \quad U &= H - PV \\
&= \frac{AS^2}{N}\ln\left(\frac{P}{P_o}\right) - PV \\
&= \frac{AS^2}{N}\ln\left(\frac{P}{P_o}\right) - \frac{AS^2}{N} \\
&= \frac{AS^2}{N}\left(\ln\left(\frac{P}{P_o}\right) - 1\right) \\
&= \frac{AS^2}{N}\left(\ln\frac{AS^2}{NVP_o} - 1\right). \\
\Rightarrow \quad T &= \left(\frac{\partial U}{\partial S}\right)_N \\
&= \frac{2AS}{N}\left(\ln\frac{AS^2}{NVP_o} - 1\right) \\
&+ \frac{AS^2}{N}\cdot\frac{NVP_o}{AS^2}\cdot\frac{2AS}{NVP_o} \\
&= \frac{2AS}{N}\ln\frac{AS^2}{NVP_o}.
\end{aligned}$$

Finalmente

$$\begin{aligned}
C_v &= \frac{T}{N}\left(\frac{\partial S}{\partial T}\right)_V \\
&= \frac{T}{N}\frac{1}{\left(\frac{\partial T}{\partial S}\right)_V} \\
&= \frac{T}{N}\frac{1}{\frac{2A}{N}\ln\frac{P}{P_o} + \frac{2AS}{N}\cdot\frac{2}{S}} \\
&= \frac{T}{2A\left(\ln\frac{P}{P_o} + 2\right)}
\end{aligned}$$