Homework 7 Solutions

Schroeder Ch. 3

3.36, 3.37, 5.5, 5.6, 5.16

Carter Ch. 8, 9

8.3, 8.4, 9.1, 9.2

+ Additional Problems 1 & 2

Schroeder

3.36 a. $S = kq\ln\left(1+\frac{N}{q}\right) + kN\ln\left(1+\frac{q}{N}\right)$

$$\frac{\partial S}{\partial N} = kq\,\frac{1}{1+\frac{N}{q}}\cdot\frac{1}{q} + k\ln\left(1+\frac{q}{N}\right) + kN\left(\frac{1}{1+\frac{q}{N}}\right)\left(\frac{-q}{N^2}\right)$$

$$= k\left(\frac{q}{q+N}\right) + k\ln\left(1+\frac{q}{N}\right) - k\,\frac{q}{N+q}$$

$$= k\ln\left(1+\frac{q}{N}\right)$$

$$\mu = -T\frac{\partial S}{\partial N} = -kT\ln\left(1+\frac{q}{N}\right)$$

b. When $N \gg q$, the logarithm is $\approx \frac{q}{N}$, so $\mu \approx -kTq/N$. This says that when we add a "particle" to the system but no energy, the entropy in fundamental units increases by $\frac{q}{N} << 1$. When $N << q$, the logarithm $\approx \ln\left(\frac{q}{N}\right)$, so $\mu \approx -kT \ln(q/N)$ and therefore, when we add a particle to the system but no energy, the entropy in fundamental units increases by $\ln(q/N)$ which is somewhat larger than 1.

When there's already a large excess of particles over energy, adding another particle doesn't increase the entropy by much. But when there's an excess of energy units over particles, adding another particle gives a significant increase in entropy. The system wants to gain particles more in the second case than the first.

3.37 a. $U = U_{kinetic} + Nmgz$

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V} = -kT\ln\left[\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right] + mgz$$

b. $\mu_0 = \mu_z$

$$-kT\ln\left[\frac{V}{N_0}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right] = -kT\ln\left[\frac{V}{N_z}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right] + mgz$$

$$\ln\left[\frac{V}{N_0}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right] = \ln\left[\frac{V}{N_z}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right] - \frac{mgz}{kT}$$

$$\frac{\cancel{V}}{N_0}\cancel{\left(\frac{2\pi mkT}{h^2}\right)^{3/2}} = \frac{\cancel{V}}{N_z}\cancel{\left(\frac{2\pi mkT}{h^2}\right)^{3/2}} \cdot e^{-mgz/kT}$$

$$N_z = N_0 e^{-mgz/kT}$$

5.5 a. $\Delta H = 2(-285.83\text{ kJ}) + (-393.51\text{ kJ}) - (-74.81\text{ kJ})$

$= -890.36\text{ kJ}$

$\Delta G = 2(-237.13\text{ kJ}) + (-394.36\text{ kJ}) - (-50.72\text{ kJ})$

$= -817.90\text{ kJ}$

d. $V = \frac{W}{q} = \frac{818\text{ kJ}}{8 \cdot 6.02 \cdot 10^{23} \cdot e}$

$= 1.06\text{ V}$

b. $G \rightarrow$ Work. $W = 818\text{ kJ}$

c. $-\Delta H = W + Q$ $\quad 890.36\text{ kJ} = 818\text{ kJ} + Q$ $\quad Q = 72\text{ kJ}$

5.6 a. $\Delta H = 6 \cdot (-393.5) + 6(-285.8) - (-1273)$

$\Delta H = -2803\ kJ$ per mole of glucose.

$\Delta G = 6 \cdot (-394.4) + 6(-237.1) - (-910) = -2879\ kJ$

b. $-\Delta G = W = 2879\ kJ$ per mole of glucose

c. $Q = W + \Delta H = 2879 - 2803 = 76\ kJ$

d. $S_{reactants} = 1442$

$S_{products} = 1704$

$\Delta S = +262\ J/K$

$Q = \Delta S \cdot T = 262\,J/K \cdot 298\,K = 78\,kJ$

Because the system gains entropy heat can flow into the system. In the ideal case, $Q = \Delta S \cdot T$.

e. Nonideal $\Rightarrow$ New entropy created during the reaction, which allows less heat to enter (or even requiring that heat be expelled, if the entropy created exceeds 262 J/K. Therefore, less energy would ~~a~~ leave the system as "other" work. ΔH & ΔG are unchanged, however.

5.16 $\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$ $\kappa_S = \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_S$

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

$dT = \left(\frac{\partial T}{\partial P}\right)_S dP + \left(\frac{\partial T}{\partial S}\right)_P dS$

Substitute dT into (1.):

$$dV = \left[\left(\frac{\partial V}{\partial P}\right)_T + \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_S\right] dP + \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial S}\right)_P dS$$

Evidently

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

, which is a form of the Clint Eastwood relation.

In terms of κ & β:

$$-V\kappa_S = -V\kappa_T + V\beta\left(\frac{\partial T}{\partial P}\right)_S$$

$$\kappa_T - \kappa_S = \beta\left(\frac{\partial T}{\partial P}\right)_S$$

However, one of our Maxwell relations tells us that $\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$

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

(chain rule)

$$\left(\frac{\partial T}{\partial P}\right)_S = \beta V \cdot \frac{T}{C_P}$$

$$\Longrightarrow$$

$$\kappa_T - \kappa_S = \frac{TV\beta^2}{C_P}$$

Ideal gas: $\kappa_T = \frac{1}{P}$ $\kappa_S = \frac{1}{\gamma P}$

$$\kappa_T - \kappa_S = \frac{1}{P}\left(1 - \frac{1}{\gamma}\right) = \frac{1}{P}\left(1 - \frac{f}{f+2}\right)$$

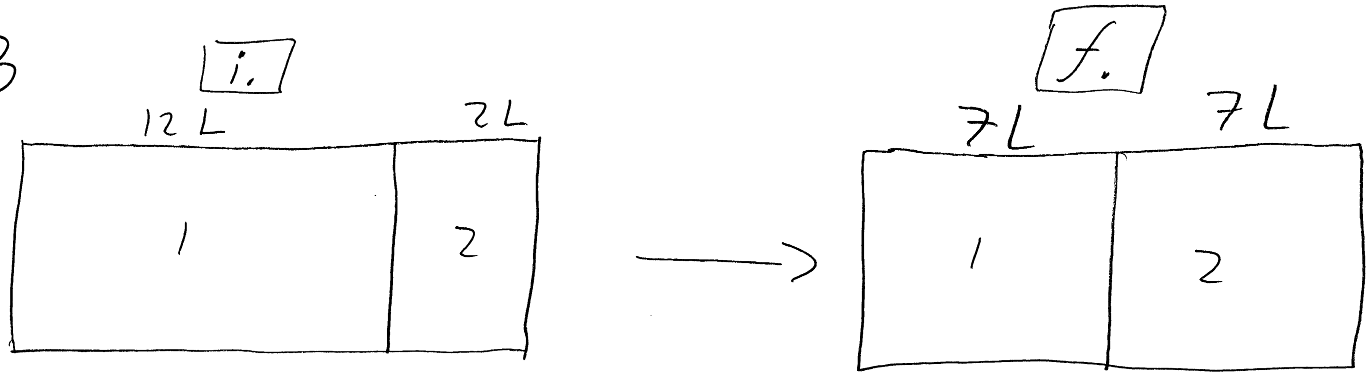
$$= \frac{1}{P}\left(\frac{2}{f+2}\right)$$

Meanwhile: $\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{V}\frac{\partial}{\partial T}\left(\frac{NkT}{P}\right)$

$C_P = \left(\frac{f+2}{2}\right) Nk$ $\beta = \frac{Nk}{PV} = \frac{1}{T}$ so

$$\frac{TV\beta^2}{C_P} = \frac{TV/T^2}{Nk}\left(\frac{2}{f+2}\right) = \frac{1}{P}\left(\frac{2}{f+2}\right) = \kappa_T - \kappa_S \checkmark$$

8.3



$T = T_0 = T_f = 273\ K \Rightarrow \Delta U = 0\ ;\ n_1 = n_2 = 1000\ mol$

$dF = -P_1\, dV_1 - P_2\, dV_2 \qquad P_1 = \frac{n_1 RT}{V_1} \quad P_2 = \frac{n_2 RT}{V_2}$

$$\Delta F = \int_i^f dF = -\int_{V_{i1}}^{V_{f_1}} \frac{n_1 RT}{V_1}\, dV_1 - \int_{V_{i2}}^{V_{f_2}} \frac{n_2 RT}{V_2}\, dV_2$$

$$= -n_1 RT \ln\left(\frac{7}{12}\right) - n_2 RT \ln\left(\frac{7}{2}\right)$$

$$= -1000 \cdot 8.315 \cdot 273 \left[\ln\left(\frac{7}{12}\right) + \ln\left(\frac{7}{2}\right)\right]$$

$$\Delta F = -1.62 \cdot 10^6$$

8.4 a, $dF = -S\, dT - P\, dV$

$$\Rightarrow \left(\frac{\partial F}{\partial T}\right)_V = -S$$

$$F = U - TS = U + T\left(\frac{\partial F}{\partial T}\right)_V$$

✓

b. $C_V = \left(\frac{\partial U}{\partial T}\right)_V$

$$F = U + T\left(\frac{\partial F}{\partial T}\right)_V$$

$$\left(\frac{\partial F}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial T}{\partial T}\right)_V\left(\frac{\partial F}{\partial T}\right)_V + T\left(\frac{\partial^2 F}{\partial T^2}\right)_V$$

$$\cancel{\left(\frac{\partial F}{\partial T}\right)_V} = \left(\frac{\partial U}{\partial T}\right)_V + \cancel{\left(\frac{\partial F}{\partial T}\right)_V} + T\left(\frac{\partial^2 F}{\partial T^2}\right)_V$$

$$-\left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial^2 F}{\partial T^2}\right)_V$$

$$\left(\frac{\partial U}{\partial T}\right)_V = -T\left(\frac{\partial^2 F}{\partial T^2}\right)_V$$

c. $dG = -S\,dT + V\,dP$

$$\Rightarrow \left(\frac{\partial G}{\partial T}\right)_P = -S$$

$$H = U + PV = G + TS = G - T\left(\frac{\partial G}{\partial T}\right)_P$$

d. $C_p = \left(\frac{\partial H}{\partial T}\right)_p$

$$H = G + TS = G - T\left(\frac{\partial G}{\partial T}\right)_p$$

$$\left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{\partial G}{\partial T}\right)_p - \left(\frac{\partial T}{\partial T}\right)_p\left(\frac{\partial G}{\partial T}\right)_p - T\left(\frac{\partial^2 G}{\partial T^2}\right)_p$$

$$= \cancel{\left(\frac{\partial G}{\partial T}\right)_p} - \cancel{\left(\frac{\partial G}{\partial T}\right)_p} - T\left(\frac{\partial^2 G}{\partial T^2}\right)_p$$

$$\left(\frac{\partial H}{\partial T}\right)_p = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_p$$

9.1 a. $dU = TdS - PdV + \mu dn$

U scales linearly with system size, as do S, V, & n. If we double the system size, we double $U, S, V, \& n$ (all are extensive). Therefore

$$2U = U(2S, 2V, 2n) \Rightarrow$$
$$\lambda U = U(\lambda S, \lambda V, \lambda n)$$

Moreover, we know from dU that $\left(\frac{\partial U}{\partial S}\right)_{V,n} = T$, $\left(\frac{\partial U}{\partial V}\right)_{S,n} = -P$,

and $\left(\frac{\partial U}{\partial n}\right)_{S,V} = \mu$.

By Euler's theorem, then, with $(x,y,z) = (S,V,n)$, we have:

$$U = ST - PV + n\mu$$

b. $dG = -SdT + VdP + \mu dn \Rightarrow$

$$\left(\frac{\partial G}{\partial n}\right)_{T,P} = \mu$$

c. $dF = -SdT - PdV + \mu dn \Rightarrow$

$$\left(\frac{\partial F}{\partial n}\right)_{T,V} = \mu$$

$$\frac{G}{n} = \mu = C_p T - C_v T \ln T - RT \ln V - s_0 T + g_0$$

where $s_0 = \frac{S_0}{n}$ ← Extensive

Intensive

$$\Longrightarrow$$

$$\mu = C_p T - C_v T \ln T - RT \ln V - s_0 T + \text{constant}$$

b. $$T\,ds = C_p\,dT - T\left(\frac{\partial v}{\partial T}\right)_P dP \; ; \; v = \frac{RT}{P}$$

$$T\,dS = n \cdot C_p\,dT - T\frac{R \cdot n}{P}$$

$$\Delta S = n C_p \ln T - nR \ln P + S_0$$

$$G = n C_v T - T(n C_p \ln T - nR \ln P + S_0) + nRT + G_0$$

$$\mu = \frac{G}{n} = C_p T - C_p T \ln T + RT \ln P - s_0 T + g_0$$

$$\Longrightarrow$$

$$\mu = C_p T - C_p T \ln T + RT \ln P - s_0 T + \text{constant}$$

$$\left(\frac{\partial \mu}{\partial P}\right)_T = \frac{RT}{P} \Longrightarrow \Delta\mu = \int_0^f \frac{RT}{P}\,dP = RT \ln\left(\frac{P_f}{P_0}\right)$$

9.2 a. $T\,ds = c_v\,dT + T\left(\frac{\partial P}{\partial T}\right)_v dv$

(Intensive variables; $s = \frac{S}{n}$ & $v = \frac{V}{n}$)

$$\left(\frac{\partial P}{\partial T}\right)_v = \frac{\partial}{\partial T}\left(\frac{RT}{v}\right) = \frac{R}{v}$$

$$T\,dS = nc_v\,dT + nT \cdot \frac{R}{V}\,dv$$

$$T\,dS = nc_v\,dT + \frac{nRT}{V}\,dV$$

(Extensive variables S, V)

$$\Delta S = nc_v \ln\left(\frac{T}{T_0}\right) + nR\ln\left(\frac{V}{V_0}\right)$$

$$= nc_v \ln T + nR\ln V + S_0$$

$$G = U - T\Delta S + PV + G_0$$

$$G = U - T(nc_v \ln T + nR\ln V + S_0) + PV + G_0$$

$$= nc_vT - nc_vT\ln T - nRT\ln V - S_0T + nRT + G_0$$

We can combine the nc_vT & nRT terms to yield $n(c_v + R)T = nc_pT$.

$$G = nc_pT - nc_vT\ln T - nRT\ln V - S_0T + G_0$$

$\mu = \Delta\mu + \mu_0$

$$\mu = RT \ln\left(\frac{P_f}{P_0}\right) + \mu_0$$

Additional Problems

1. $dS = \frac{1}{T} dU + \frac{P}{T} dV - \frac{\mu}{T} dN$

a. Let $S' = S - \frac{U}{T}$

Then

$$dS' = dS - \frac{1}{T} dU - U\, d\left(\frac{1}{T}\right)$$

$$= \cancel{\frac{1}{T} dU} + \frac{P}{T} dV - \frac{\mu}{T} dN - \cancel{\frac{1}{T} dU} - U\, d\left(\frac{1}{T}\right)$$

$$dS' = \frac{P}{T} dV - \frac{\mu}{T} dN - U\, d\left(\frac{1}{T}\right)$$

b. Let $S'' = S' - \frac{P}{T} V = S - \frac{U}{T} - \frac{PV}{T}$

$$dS'' = dS' - \frac{P}{T} dV - V\, d\left(\frac{P}{T}\right)$$

$$= \cancel{\frac{P}{T} dV} - \frac{\mu}{T} dN - U\, d\left(\frac{1}{T}\right) - \cancel{\frac{P}{T} dV} - V\, d\left(\frac{P}{T}\right)$$

$$\boxed{dS'' = -\frac{\mu}{T}\,dN - U\,d\left(\frac{1}{T}\right) - V\,d\left(\frac{P}{T}\right)}$$

c. Let

$$\boxed{\begin{aligned} S''' &= S' + \frac{\mu}{T}N \\ &= S - \frac{U}{T} + \frac{\mu}{T}N \end{aligned}}$$

$$dS''' = dS' + \frac{\mu}{T}\,dN + N\,d\left(\frac{\mu}{T}\right)$$

$$= \frac{P}{T}\,dV - \cancel{\frac{\mu}{T}\,dN} - U\,d\left(\frac{1}{T}\right) + \cancel{\frac{\mu}{T}\,dN}$$

$$+ N\,d\left(\frac{\mu}{T}\right)$$

$$\boxed{dS''' = \frac{P}{T}\,dV - U\,d\left(\frac{1}{T}\right) + N\,d\left(\frac{\mu}{T}\right)}$$

2. ~~[illegible]~~

~~[illegible]~~

See Solution Supplement