HW#7 Yang Yang

3.25 5.14. 5.15 5.23.

3.25 a) $S = k\ln\Omega = k\ln\left(\frac{q+N}{q}\right)^q + k\ln\left(\frac{q+N}{N}\right)^N$

$$= \boxed{kq\ln\left(\frac{q+N}{q}\right) + kN\ln\left(\frac{q+N}{N}\right)}$$

The omitted factors in Ω were of order $\sqrt{N}\cdot\sqrt{q}$. The logarithm of such factor is small, compared with q or N.

b) $\frac{1}{T} = \frac{\partial S}{\partial U} = \frac{\partial q}{\partial U}\frac{\partial S}{\partial q} = \frac{1}{\epsilon}\frac{\partial S}{\partial q}$

$$= \frac{k}{\epsilon}\frac{\partial}{\partial q}\left[q\ln(q+N) - q\ln q + N\ln(q+N) - N\ln N\right]$$

$$= \frac{k}{\epsilon}\left[\ln(q+N) + \frac{q}{q+N} - \ln q - \frac{q}{q} + \frac{N}{q+N}\right]$$

$$= \frac{k}{\epsilon}\left[\ln\left(\frac{q+N}{q}\right)\right]$$

$$\boxed{T = \frac{\epsilon}{k\ln(1+N\epsilon/U)}}$$

c) $U = \frac{N\epsilon}{e^{\epsilon/kT}-1}$

$$\boxed{C = \frac{\partial U}{\partial T} = \frac{N\epsilon^2}{kT^2}\frac{e^{\epsilon/kT}}{(e^{\epsilon/kT}-1)^2}}$$

d) $T\to\infty$ $\frac{\epsilon}{kT}\ll 1$ $e^{\epsilon/kT} = 1+\epsilon/kT$

$$C = \frac{N\epsilon^2}{kT^2}\cdot\cancel{e}\frac{1}{(\epsilon/kT)^2} = Nk$$

Each oscillator counts as two degrees of freedom. just as the equipartition theorem.

f) $e^x \approx 1 + x + \frac{1}{2}x^2 + \frac{1}{6}x^3 + \cdots$

$$\frac{C}{Nk} = \frac{x^2 e^x}{(e^x-1)^2} \approx \frac{x^2(1+x+\frac{1}{2}x^2+\frac{1}{6}x^3)}{(x+\frac{1}{2}x^2+\frac{1}{6}x^3)^2}$$

$$\approx \frac{1+x+\frac{1}{2}x^2+\frac{1}{6}x^3}{(1+\frac{1}{2}x+\frac{1}{6}x^2)^2} \approx \frac{1+x+\frac{1}{2}x^2}{1+x+\frac{1}{4}x^2+\frac{1}{3}x^2}$$

$$= \frac{1+x+\frac{1}{2}x^2}{1+x+\frac{7}{12}x^2}$$

$$\approx 1 - \frac{1}{12}x^2$$

$$C = Nk\left[1 - \frac{1}{12}x^2 + \cdots\right] = Nk\left[1 - \frac{1}{12}\left(\frac{kT}{\epsilon}\right)^2 + \cdots\right]$$

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

The partial derivative in the first term is C_V/T

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

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

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

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

$$\left.\begin{aligned} C_P &= T\left(\frac{\partial S}{\partial T}\right)_P \\ C_V &= T\left(\frac{\partial S}{\partial T}\right)_V \end{aligned}\right\} \Rightarrow C_P = C_V + T\left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

c) Maxwell relation $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

$$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P = T\left[-\frac{(\partial V/\partial T)_P}{(\partial V/\partial P)_T}\right]\left(\frac{\partial V}{\partial T}\right)_P$$

$$= -T\left(\frac{\partial V}{\partial T}\right)_P^2 \Big/ \left(\frac{\partial V}{\partial P}\right)_T$$

$$\beta \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad \kappa_T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

So $C_P - C_V = \dfrac{TV\beta^2}{\kappa_T}$

d) For an ideal gas

$$\beta = \frac{1}{V}\left(\frac{Nk}{P}\right) = \frac{1}{T}$$

$$\kappa_T = -\frac{1}{V}\left(-\frac{NkT}{P^2}\right) = \frac{1}{P}$$

$$C_P - C_V = Nk$$

e) $\beta^2 > 0$ $\quad$ κ_T can ~~never~~ never be negative since adding pressure will always decrease pressure.

$$\boxed{C_P > C_V}$$

f) For one gram of water, at room temperature.

$$C_P - C_V = \frac{(298\,K)(10^{-6}m^3)(2.57\times10^{-4}K^{-1})^2}{4.52\times10^{-10}Pa^{-1}} = 0.0435\,J/K$$

over 1% of the heat capacity.

For one mole of mercury

$$C_P - C_V = \frac{(298K)(14.8\times10^{-6} m^3)(1.81\times10^{-4} K^{-1})^2}{4.04\times10^{-11} Pa^{-1}} = 3.58 J/K$$

$\approx 13\%$ op the C_P (28.0 J/K)

a) For solid $\kappa_T \approx$ const so $C_P - C_V \propto T\beta^2$

when $T \to 0$ $\beta(T)$ also $\to 0$ $\beta^2 T \to 0$. $C_P - C_V \to 0$

At high temperature $\beta(T) \to$ const $C_P - C_V \propto T$

5.15

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

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP \quad ②$$

plug ② to ① $dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T \left[\left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP\right]$

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

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial (U+PV)}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P$$

$$C_P - C_V = \left(\frac{\partial V}{\partial T}\right)_P \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]$$

Rewrite P as $-(\partial F/\partial V)_T$ $\quad U - F = TS$

So $\left(\frac{\partial U}{\partial V}\right)_T + P = \left(\frac{\partial U}{\partial V}\right)_T - \left(\frac{\partial F}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T$

$$\Rightarrow C_P - C_V = T\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial S}{\partial V}\right)_T$$

5.23 a) $\Phi = U - TS - \mu N$

$$d\Phi = dU - TdS - SdT - \mu dN - Nd\mu$$

$$= -SdT - PdV - Nd\mu$$

$$\left(\frac{\partial \Phi}{\partial T}\right)_{V,\mu} = -S \qquad \left(\frac{\partial \Phi}{\partial V}\right)_{T,\mu} = -P \qquad \left(\frac{\partial \Phi}{\partial \mu}\right)_{T,V} = -N$$

b) The total entropy for the system is the ~~sumation~~ summation of the system and the reservoir

$$dS_{total} = dS + dS_R$$

Assuming the V of the reservoir is fixed.

$$dS_R = \frac{1}{T}dU_R - \frac{\mu}{T}dN_R$$

$$dU + dU_R = 0 \qquad dN + dN_R = 0 \qquad dS_R = -\frac{1}{T}dU + \frac{\mu}{T}dN$$

$$dS_{total} = dS - \frac{1}{T}dU + \frac{\mu}{T}dN = -\frac{1}{T}(dU - TdS - \mu dN) = -\frac{1}{T}d\Phi$$

Since $dS_{total} > 0$

$d\Phi < 0$ $\quad \Phi$ tends to decrease.

c) $\Phi = U - TS - \mu N = U - TS + PV - PV - \mu N = G - PV - \mu N = -PV$

$(G = \mu N)$

d) For unoccupied state

$U = S = N = 0$

$$\boxed{\Phi = 0}$$

For the occupied state $S=0$ $N=1$

$$\Phi_{oc} = U_0 - \mu = U_0 + kT\ln\left[\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right]$$

$$= -13.6eV + (8.62\times10^{-5}eV/k)\cdot(5800K)\cdot\ln\left[0.5\times10^{-10}m^3\cdot\left(\frac{2\pi\cdot(9.11\times10^{-31}kg)\cdot(1.38\times10^{-23}J/k)\cdot(5800k)}{(6.63\times10^{-34}J\cdot S)^2}\right)^{3/2}\right]$$

$$= -4.7eV$$

To get a rough estimation, we assume the logarithm part is a constant $\Phi_{oc}=0 \Rightarrow T = 8800K$.

$$\left(\ln\left[\frac{V}{N}\left(\frac{2\pi mk}{h^2}\right)^{3/2}\right] \text{ is much larger than } \ln[T^{3/2}]\right)$$