1st Physical Chemistry Midterm Exam, 6th October 2005

$4 + 5 + 5 + 5 + 4 = 23$ points, 20 points = 100%

1. State Postulate II of Callen. In the internal energy representation, what is the equivalent of the entropy maximum principle? Formulate mathematically what the entropy *maximum* means for a simple system. *(4 points)*

2. Is the following equation of a simple system consistent with Postulates II-IV?

$$S = (R/\theta)^{1/2}(NU)^{1/2} \exp\left(-\frac{UV}{NR\theta v_0}\right)$$

   R, θ and v_0 are positive constants, and only the real positive root is to be taken when fractional exponents appear. *(5 points)*

3. Calculate the quasi-static heat for the following process. The system is initially at state A ($P_A = 10^3$ Pa) and quasi-statically moves along the line $P/\text{Pa} = ((V-2)/\text{m}^3)^3$. The final state is B ($P_B = 8 \times 10^3$ Pa). Points A and B also lie on the adiabat of this particular system, and if the pressure changes along this adiabat, the work done is -15 kJ. *(5 points)*

4. Two isolated cylinders (A and B) are separated by a wall, which is diathermal, moveable, but impermeable with respect to matter. Cylinder A is filled with a monatomic ideal gas ($f_1 = 3$), while cylinder B is filled with a diatomic ideal gas ($f_2 = 5$). Initially the two systems are at equilibrium: U_A=10 kJ, V_A=5 dm^3, N_A=3, and N_B=2.

   (a) Calculate the volume of cylinder B. *(2.5 points)*

   (b) Subsequently 3 kJ heat is introduced in cylinder A by means of an electric wire. Calculate the temperature and the pressure at the new equilibrium. *(2.5 points)*

   The internal energy of ideal gases is $U = \frac{f}{2}PV$.

5. A system obeys the two equations $u = 3/2Pv$ and $u^{1/2} = BTv^{1/3}$. Find the extensive fundamental equation of the system (B is a constant). *(4 points)*

$R = 8.314 \frac{\mathrm{J}}{\mathrm{mol\,K}} \qquad N_A = 6.022 \cdot 10^{23} \qquad k = 1.38 \cdot 10^{-23}\,\mathrm{J\,K^{-1}} \qquad g = 9.81 \mathrm{m\,s^{-2}}$

$1\mathrm{P} = 0.1\mathrm{Pa\ s^{-1}} \qquad 1\,\mathrm{atm} = 101325\,\mathrm{Pa} \qquad 1\,\mathrm{bar} = 10^5\,\mathrm{Pa}$

$U = \frac{3}{2} NRT \qquad U = \frac{5}{2} NRT$

$PV = NRT$

$dU = đW + đQ \qquad đW = -P\,dV \qquad đQ = T\,dS$

$\eta = 1 - \frac{T_c}{T_h}$

$dU = T\,dS - P\,dV + \sum_i \mu_i\,dN_i \qquad dS = \frac{1}{T}\,dU + \frac{P}{T}\,dV - \sum_i \frac{\mu_i}{T}\,dN_i$

$S\,dT - V\,dP + \sum_i N_i\,d\mu_i = 0 \qquad U\,d\frac{1}{T} + V\,d\frac{P}{T} - \sum_i N_i\,d\frac{\mu_i}{T} = 0$

$H = U + PV \qquad F = U - TS \qquad G = U - TS + PV$

$H = \left(\frac{\partial(G/T)}{\partial(1/T)}\right)_P$

$\left(\frac{\partial\mu}{\partial T}\right)_P = -s \qquad \left(\frac{\partial\mu}{\partial P}\right)_T = v$

$\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$

$\kappa_T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \qquad \kappa_s \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S$

$c_P \equiv \frac{T}{N}\left(\frac{\partial S}{\partial T}\right)_P = \frac{1}{N}\left(\frac{\partial Q}{\partial T}\right)_P$

$c_v \equiv \frac{T}{N}\left(\frac{\partial S}{\partial T}\right)_V = \frac{1}{N}\left(\frac{\partial Q}{\partial T}\right)_V$

$c_P = c_v + \frac{TV\alpha^2}{N\kappa_T} \qquad \kappa_T = \kappa_s + \frac{TV\alpha^2}{Nc_P}$