Chemistry 301
Thermodynamics
Midterm Exam
Part B
October 6, 1993

Name ___________

Full credit will be given to correct answers only when ALL the necessary steps are shown. DO NOT GUESS THE ANSWER.

This is a open book open notes exam, and you are responsible to be sure that your exam has no missing pages(5 pages).

If you consider that there is not enough information to solve a problem, you have to specify the missing information and describe the problem solving procedure.

But surely this is an old tale you tell, they say;
But surly this is a new tale you tell, other say.
Tell it once again, they say;
Or, do not tell it yet again, others say.
But I have heard all this before, say some;
Or, but this is not how it was before, say the rest

Naqshbandi recital, from The Way of the Sufi, by Idries Shah

Once you start the exam, you have up to 24 hours to solve it.

Starting time: _______________________

Ending time: ________________________

Honor Statement

I have neither give nor received aid in this examination.

Full signature ________________________________

Problem 1.-

a)(5 points)

Find the final temperature of two liters of water when we mix one liter at 100 °C and one liter at 20 °C.

b)(5 points)

Now instead of mixing two liters, we drop a chunk of 1000 g of copper at 100 °C in the one liter of water at 20 °C.. Find the final temperature of the system copper-water.

c) (5 points)

Finally, we drop 1000 g of ice at 0 °C in the one liter of water at 20 °C. Find the temperature of the system ice-water.

[Assume insulated containers.]

Problem 2.(40 points)

Consider a fused salt alkali halide consisting of N/2 cations and N/2 anions in a total volume V. The number density r is given by N/V and the molecular volume by *v* by V/N. Assuming equal-size anions and cations of diameter σ, the packing fraction y is given by

π

σ

Error!

$$P = \rho k_B T \frac{1 + y + y^2 - y^3}{(1 - y)^3} - \frac{A \rho^{4/3}}{3} .$$

Here A is a constant independent of temperature and density. Years ago, McQuarrie[2] arrived at a similar expression for the pressure in a fused salt using cell theory. In this case, y may have density dependence but it is likely to be much less than its temperature dependence. Consequently, we shall ignore any term involving $\left(\frac{\partial y}{\partial \rho}\right)_T$. Two equations can be derived from the equation of state[3] .

These two relations are: isothermal compressibility

$$\kappa_T = \frac{1}{\rho \left(\frac{\partial \rho}{\partial P}\right)_{NT}} ,$$

and the thermal pressure coefficient

$$\gamma_\rho = \left(\frac{\partial P}{\partial T}\right)_\rho .$$

Calculate $1/\kappa_T$.

References

1. Itami, T. and Shimoji, J. Chem. Soc., Faraday Trans. 2, **76**, 1347 (1980)
2. McQuarrie, D. A., J. Phys. Chem., **66**, 1508 (1961).
3. McBroom, R. B. and McQuarrie, D. A., J. Phys. Chem., **87**, 3171 (1983)

Problem 3.(45 points)

Consider the following cycle for one mole of ideal gas

Step 1.- Isothermal reversible expansion from V_1 to V_2 at $T = T_h$.
Step 2 .- Adiabatic reversible expansion from V_2 to V_3 and $T = T_h$ to $T = T_c$.
Step 3 .- Isothermal reversible compression from V_3 to V_4 at $T = T_c$.
Step 4 .- Adiabatic reversible compression from V_4 to V_1 and $T = T_c$ to $T = T_h$

a) **(5 points)** Sketch the cycle in P-V space

Assume that the values of R, C_V, C_P, V_1, V_2, V_3, V_4, T_h, and T_c are known.

b) **(5 points)** For Step 1, calculate the work done by the system (W_1) and the heat exchanged with the surroundings (q_h) as functions of V_1, V_2 and T_h.

c) **(5 points)** For Step 2, calculate the work done by the system (W_2) and the heat exchanged with the surroundings (q_2) as functions of T_h and T_c.

d) **(5 points)** For Step 3, calculate the work done by the system (W_3) and the heat exchanged with the surroundings (q_c) as functions of V_3, V_4 and T_c.

e) **(5points)** For Step 4, calculate the work done by the system (W_4) and the heat exchanged with the surroundings (q_4) as functions of T_h and T_c.

f) **(5 points)** Calculate the net work ($W_{net} = W_1 + W_2 + W_3 + W_4$) for the cycle.

The efficiency of the cycle (ε) is defined as

$$\varepsilon = \frac{-W_{net}}{q_h}.$$

g) **(5 points)** Using your previous results, prove that the efficiency can be express as

$$\varepsilon = 1 + \frac{q_c}{q_h}.$$

h) **(5 points)** It can also be express as

$$\varepsilon = 1 - \frac{T_c}{T_h} \ .$$

i) **(5 points)** Finally, prove that the integral

$$\oint \frac{dq}{T} = \int_{Step\,1} \frac{dq}{T} + \int_{Step\,2} \frac{dq}{T} + \int_{Step\,3} \frac{dq}{T} + \int_{Step\,4} \frac{dq}{T}$$

is zero for the cycle.

Bonus (10 points)(no partial credit)

Can an irrational number to an irrational power be a rational number?