PHY 3513 Fall 2000 – Information Concerning Mid-Term Exam 1

The first mid-term will take place between 7:00 and 9:00 pm on Tuesday October 17. The exam will be held in room NPB 1220.

The exam will consist of three questions carrying roughly equal weight (e.g., 40%, 30%, and 30%). One question will be devoted to each of the following areas:

- Introductory material on heat, work, and energy; their relation via the First Law; heat capacities and latent heats; application of the preceding ideas to ideal gases; the kinetic theory of gases; entropy and the second law. The statistical interpretation of entropy will not be tested.
- Callen Chapter 1, Sections 3–6, and 8–10: Extensive variables, systems and walls, equilibrium states, the entropy postulates.
- Callen Chapter 2, Sections 1–8: Intensive variables, equations of state, thermal, mechanical and diffusional equilibrium between subsystems.

You should bring a scientific calculator and pens/pencils to the exam. You will be provided with a formula sheet (attached); no other written aids will be allowed.

Below is the first PHY 3513 mid-term from 1999. The format of the exam is slightly different (four problems instead of three), but the type of questions is representative of those that will appear this time.

PHY 3513 Fall 1999 – Mid-Term Exam 1

This exam lasts 2 hours. Answer all four questions, which carry equal weight. To obtain full credit, please explain your reasoning and show all working. Please write neatly and include your name on the front page of your answers.

You must not seek or obtain help on this exam from anyone other than the proctor, nor must you assist anyone else.

1. The low-temperature heat capacity of a certain sample of solid argon is described by the formula $C_{\text{Ar}} = \alpha T^3$. Over the same temperature range, the heat capacity of a piece of potassium is given by $C_{\text{K}} = \gamma T + \beta T^3$. The constants α, β, and γ are all positive.

   Initially, the argon and potassium are held at temperatures T_{Ar} and T_{K}, respectively. Then the two samples are brought into thermal contact and allowed to equilibrate.

   (a) Obtain an expression for T_f, the final temperature of the argon and the potassium, assuming that the two samples together form a closed system. [Hint: During the calculation, you should solve a quadratic equation for T_f^2. Be sure to specify which root of the equation is the physical one.]

   (b) Evaluate T_f, given that $\alpha = 3.0 \times 10^{-3}\,\text{J/K}^4$, $\beta = 2.1 \times 10^{-3}\,\text{J/K}^4$, $\gamma = 2.6 \times 10^{-3}\,\text{J/K}^2$, $T_{\text{Ar}} = 0.35\,\text{K}$, and $T_{\text{K}} = 1.6\,\text{K}$.

2. A certain gas of non-interacting molecules satisfies the pair of equations $u = cRT$ and $P(v - b) = RT$, where u is the molar internal energy, v is the molar volume, T is the absolute temperature, P is the absolute pressure, R is the gas constant, and c is a dimensionless constant greater than unity. The second equation can be derived from

kinetic theory, treating each molecule not as a point-like particle, but rather as an object having a finite volume of order b/N_A (where N_A is Avogadro's constant).

Calculate the increase in the molar entropy of a fixed amount of this gas during each of the following processes:

(a) A change in temperature from T_i to T_f at constant molar volume v_0.

(b) A change in temperature from T_i to T_f at constant pressure P_0.

(c) A change in molar volume from v_i to v_f at constant temperature T_0.

The only algebraic variables in your answers should be the ones mentioned in the problem, i.e., don't introduce new variables such as P_i or P_f.

3. Suppose that the following equation has been proposed as the fundamental equation for a one-component simple thermodynamic system:

$$U(S, V, N) = NVe^S. \tag{1}$$

(a) Check whether the equation has the correct extensivity property. Remedy any deficiences by inserting powers of N as necessary on the right hand side of the equation.

(b) Check whether the equation (as corrected above, if necessary) is dimensionally correct. Remedy any deficiencies by inserting powers of R [units: J/(mol·K)], θ [units: K], and v_0 [units: m³/mol] as necessary on the right hand side of the equation.

(c) Check whether the equation (as corrected above, if necessary) satisfies each of the remaining requirements of the entropy postulates.

(d) If you find any violations of the entropy postulates, make the smallest possible change you can find to bring the equation into compliance, while maintaining extensivity and dimensional correctness. [Since the "smallest possible change" is subjective, there may not be a unique answer to this part. However, your final version of the fundamental equation should be clearly derived from Eq. (1).]

4. A closed system is composed of two simple subsystems, labeled A and B. A is a simple ideal gas, described by

$$S_A = N_A s_0 + N_A R \ln \left[\left(\frac{U_A}{U_0} \right)^c \left(\frac{V_A}{V_0} \right) \left(\frac{N_0}{N_A} \right)^{c+1} \right], \tag{2}$$

and B is a cavity containing electromagnetic radiation described by

$$S_B = \frac{4}{3} \left(b U_B^3 V_B \right)^{1/4}. \tag{3}$$

(a) Write down the equations of state for the temperature and pressure of each subsystem.

(b) Initially the subsystems are separated by an adiabatic, rigid, impermeable barrier. Then the barrier is replaced by one that is diathermal, movable, and impermeable and the combined system is allowed to reach equilibrium. Derive (and simplify, but do **not** attempt to solve) equations for $U_{A,f}$ and $V_{A,f}$, the final internal energy and volume of A, as functions of the total internal energy U, the total volume V, and constants introduced in Eqs. (2) and (3).

General equations

- Heat *into* system: $\quad\quad dQ \overset{\text{QS}}{=} TdS \quad\quad$ ("QS" means quasistatic)

- Work done *on* system: $\quad dW \overset{\text{QS}}{=} -PdV + \sum_j \mu_j dN_j + \ldots + F_k dX_k + \ldots$

- First Law: $\quad\quad\quad\quad\quad dU = dQ + dW$

- Second Law: $\quad\quad\quad\quad dS_{\text{tot}} \geq 0 \quad\quad$ ("=" for reversible processes)

Entropy postulates

- Entropy is additive over subsystems: $S = \sum_\alpha S^{(\alpha)}(U^{(\alpha)}, V^{(\alpha)}, N_1^{(\alpha)}, \ldots)$.
- Within each subsystem, the entropy is . . .
  - an extensive function of extensive variables:
    $S^{(\alpha)}(\lambda U^{(\alpha)}, \lambda V^{(\alpha)}, \lambda N_1^{(\alpha)}, \ldots) = \lambda S^{(\alpha)}(U^{(\alpha)}, V^{(\alpha)}, N_1^{(\alpha)}, \ldots)$;
  - continuous, differentiable, and monotonically increasing with respect to energy:
    $(\partial S^{(\alpha)}/\partial U^{(\alpha)})_{V^{(\alpha)}, N_1^{(\alpha)}, \ldots} > 0$;
  - non-negative, and zero only in the state for which $(\partial U^{(\alpha)}/\partial S^{(\alpha)})_{V^{(\alpha)}, N_1^{(\alpha)}, \ldots} = 0$.
- At thermodynamic equilibrium, S is maximized subject to whatever constraints are applied to the system.

Intensive parameters

- Temperature: $\quad\quad\quad T = \left(\dfrac{\partial U}{\partial S}\right)_{V, N_1, \ldots} = 1 \bigg/ \left(\dfrac{\partial S}{\partial U}\right)_{V, N_1, \ldots}$

- Pressure: $\quad\quad\quad\quad P = -\left(\dfrac{\partial U}{\partial V}\right)_{S, N_1, \ldots} = T \left(\dfrac{\partial S}{\partial V}\right)_{U, N_1, \ldots}$

- Molar chemical potential: $\quad \mu_k = \left(\dfrac{\partial U}{\partial N_k}\right)_{S, V, N_1, \ldots} = -T \left(\dfrac{\partial S}{\partial N_k}\right)_{U, V, N_1, \ldots}$

Simple one-component systems

- Molar entropy, energy, volume: $\quad s = S/N, \quad u = U/N, \quad v = V/N$

- First Law: $\quad\quad\quad\quad\quad\quad\quad du = T\,ds - P\,dv$

- Constant-X molar heat cap.: $\quad c_X = \dfrac{1}{N}\left(\dfrac{dQ}{dT}\right)_{X,N} = \dfrac{T}{N}\left(\dfrac{\partial S}{\partial T}\right)_{X,N} \quad\quad$ (e.g., $X = V$, P)

- Molar latent heat: $\quad\quad\quad l = \pm\left(\dfrac{dQ}{dN}\right)_T \quad$ during a change of phase

Ideal gases

- Equation of state: $\quad\quad PV = NRT = N_{\text{molecules}} k_B T$

- Internal energy: $\quad\quad\quad U = cNRT \quad\quad (c \geq \frac{3}{2})$

- Adiabatic processes: $\quad PV^\gamma = \text{constant}$

- Kinetic theory: $\quad\quad\quad PV = \frac{1}{3}NMv_{\text{rms}}^2 = \frac{1}{3}N_{\text{molecules}} m v_{\text{rms}}^2$