

**Pledge and signature:****I. (30) Elective Experiments. Do only ONE of the following three problems; pick one that corresponds to your lab work.** (Other choices will not be counted.)**A. Freezing Point Depression.**

- (14) A 10.00-g sample of a weak acid ( $M = 76.0$  g/mol) in water is titrated to neutrality with 19.7 mL of 0.122 M NaOH. The freezing point of this mixture is found to be  $-0.504$  °C. Calculate (a) the molality of the acid (from titration), (b) the fraction dissociated, and (c) the equilibrium constant  $K_m$ . [ $k_f = 1.860$  K kg mol<sup>-1</sup>]; treat activity coefficients = 1 here.]
- (12) A 1.500% solution of CaCl<sub>2</sub> (110.99 g/mol) in water (18.015 g/mol) has a freezing point of  $-0.661$  °C. Calculate (a) the molality of CaCl<sub>2</sub>, (b) the predicted (simple theory) freezing point, (c) the practical osmotic coefficient, and (d) the activity  $a_A$ .
- (4) (a) Suppose the freezing point given just above is uncertain by 0.005 °C. Assuming that this is the only source of experimental uncertainty, calculate the resulting uncertainty in .  
(b) Suppose the titration volume in (1) is uncertain by 0.3 mL. Again assuming that this is the only source of uncertainty, calculate the resulting uncertainty in the acid molality.

**B. Thermal Expansivity.** [Hint: Precision is *very* important in all these calculations.]

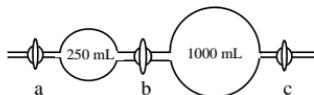
- (2) A pycnometer is fitted with a capillary extension (like those in our laboratory) having an internal diameter of 1.00 mm. In the initial calibration with water, the capillary height is 17.7 mm above the zero level. Calculate the volume of water ( $\text{cm}^3$ ) in the capillary.
- (6) The apparent mass of the empty pycnometer and capillary extension is 22.379 g. Filled with water to capillary height 17.7 mm (as above), the apparent mass is 47.912 g. At the temperature of these measurements, the density of water is  $0.998011 \text{ g/cm}^3$ . The density of air may be taken as  $1.19 \text{ mg/mL}$ . Calculate the volume  $V_0$  (*i.e.*, to the zero mark) (a) neglecting the buoyancy of air, and (b) taking it into account.
- (4) An unknown liquid is placed in this pycnometer, giving a capillary reading of 17.7 mm when the system is equilibrated at  $27.43^\circ\text{C}$ . When it is reequilibrated at  $29.12^\circ\text{C}$ , the capillary level is 47.1 mm. (a) Calculate the average  $\rho$  for this liquid over this temperature range. (b) What would be the best temperature to record for this estimate of  $\rho$ ?
- (3) If each of the capillary measurements in (3) above is uncertain by 0.3 mm, and if this is the only significant source of uncertainty, what is the % uncertainty in the estimated value of  $\rho$ ?
- (1) If the density of a fluid is represented as  $\rho = \rho_0 \exp(bx + cx^2)$ , where  $x = t(^{\circ}\text{C}) - 25^\circ\text{C}$ , what is the physical meaning of  $\rho_0$ ?

### C. Physical Adsorption.

1. (16) In an adsorption experiment, the sample cell has a volume of  $17.3 \text{ cm}^3$  and the vacuum manifold (w/ Baratron gauge)  $72.7 \text{ cm}^3$ . The manifold is charged with  $\text{N}_2$  to a pressure of  $84.1 \text{ Torr}$ . Then the valve to the cell (previously evacuated to  $P = 0$ ) is opened, with the cell containing  $1.0 \text{ cm}^3$  of silica gel and the whole system at  $T = 295 \text{ K}$ . After the new  $P$  is measured ( $P_2$ ), the cell is cooled with  $\text{LN}_2$ , dropping  $P$  to  $8.5 \text{ Torr}$  ( $P_3$ ). The "cold volume" is  $6.6 \text{ cm}^3$ . [ $R = 0.082058 \text{ L atm mol}^{-1} \text{ K}^{-1}$ ;  $1 \text{ mol} = 22\,414 \text{ STP cc}$ ;  $\text{LN}_2 T = 77 \text{ K}$ .]

Calculate: (a)  $P_2$  (in Torr); (b) the amount of  $\text{N}_2$  initially placed in the manifold, in STP cc; and (c) the amounts (STP cc) of  $\text{N}_2$  (i) adsorbed and (ii) remaining in the gas phase at the end.

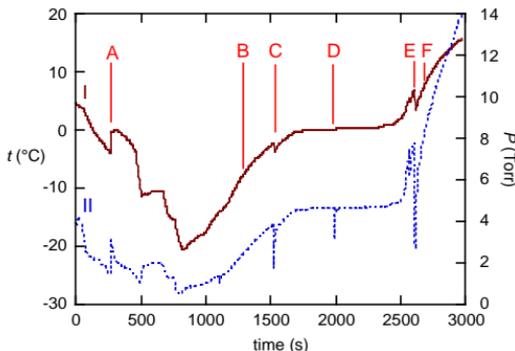
2. (5) In Denver, because of the high elevation, "atmospheric pressure" is normally about 600 torr. What would be the temperature of liquid  $\text{N}_2$  in an open Dewar at that pressure? [normal boiling point =  $77.3 \text{ K}$ ,  $H_{\text{vap}} = 5.58 \text{ kJ/mol}$ ]
3. (9) Consider the apparatus pictured to the right. Initially this system is filled with He at a pressure of 512 torr and a temperature of 301 K. Then the 250-mL bulb is immersed in  $\text{LN}_2$  at 77 K. Calculate (a) the number of moles of He present, (b) the pressure after the small bulb is cooled to 77 K, and (c) the number of moles of He in each of the two bulbs in the latter case.



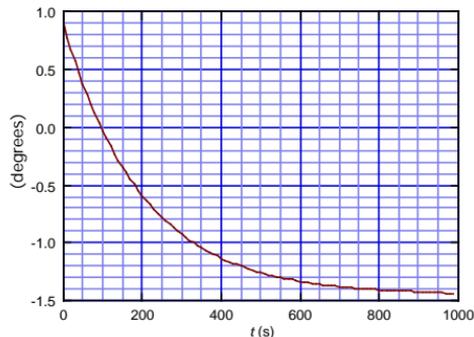
Before beginning Part II, enter here the names of your lab partners and the number of peer points you wish to award to each. The total must not exceed 24, and the maximum to any one partner is 19. If you leave this space blank, your points will be distributed 12:12.

## II. (21) Review.

- A. (6) This figure shows the time dependence of  $T$  and  $P$  in the Triple Point experiment. Tell which curve (I & II) is which, and identify (by letter) points where (1) solid, liquid, and vapor are simultaneously in equilibrium; (2) solid (only) is in equilibrium with vapor; (3) liquid (only) is in equilibrium with vapor; (4) supercooled water freezes; and (5) The valve to the pump may have been opened momentarily.



- B. (7) The figure to the right represents optical rotation data for a hypothetical sugar we shall call *picanose*. From this figure, give approximate values for the following quantities: (1)  $\alpha_0$ , (2)  $\alpha_{\infty}$ , (3) the inversion time (in s), (4) the half-life of *picanose*, and (5) the effective rate constant  $k_{\text{eff}}$ .



**C. (8) Data Analysis**

1. You desire to fit some data using the fit function,  $y = a/x^2 + bx^2$ , but you need to do this using a program that will fit data to just the straight line,  $Y = a + bX$ .
  - (a) How must you define the points,  $(X_i, Y_i)$  for the latter analysis in terms of the points  $(x_i, y_i)$  of the former?
  - (b) If the original  $y_i$  values have constant uncertainty  $\sigma_y = 1$ , how should the data in the second fit be weighted?
2. A quantity  $z$  can be expressed as a ratio of  $x$  and  $y$ ,  $z = x/y$ . The latter are obtained from measurements of  $t$ ,  $u$ , and  $v$ , using  $x = t u^2/v$  and  $y = t u v$ . Give expressions for the relative uncertainties of  $x$ ,  $y$ , and  $z$ , in terms of the relative uncertainties in  $t$ ,  $u$ , and  $v$ .