

- Calculate the entropy change of the system and the surroundings for a diatomic van der Waal's gas.
  - reversible isothermal expansion of 0.02 moles of gas from 0.5 L to 7.0 L at 300 K.
  - reversible isothermal expansion of 0.02 moles of gas from 0.5 L to 7.0 L at 500 K.
  - constant pressure expansion of 0.02 moles of gas against 0.07 atm of pressure at 300 K.
  - heating 0.02 moles of gas reversibly from 300 K to 500 K.
- A. Given the following data at 50 °C determine the activity and activity coefficient for iodoethane (I) and ethylacetate (E) at a mole fraction of  $x_E = 0.6282$ .

$x_I$	$P_I$ (torr)	$P_E$ (torr)
0.0000	0.0	280.4
0.0579	20.0	266.1
0.1095	52.7	252.3
0.1918	87.7	231.4
0.2353	105.4	220.8
0.3718	155.4	187.9
0.5478	213.3	144.2
0.6349	239.1	122.9
0.8253	296.9	66.6
0.9093	322.5	38.2
1.0000	353.4	0.000

The Henry's law constants are  $K_{H,I}$  and  $K_{H,E}$  should be calculated from the relationship:

$$P_{\text{total}} = x_I P_1^* \exp\{x_2^2/4\} + x_2 P_2^* \exp\{x_1^2/4\}$$

Henry's law standard state

$$a_I = \underline{\hspace{2cm}} \quad \gamma_I = \underline{\hspace{2cm}}$$

$$a_E = \underline{\hspace{2cm}} \quad \gamma_E = \underline{\hspace{2cm}}$$

Raoult's law standard state

$$a_I = \underline{\hspace{2cm}} \quad \gamma_I = \underline{\hspace{2cm}}$$

$$a_E = \underline{\hspace{2cm}} \quad \gamma_E = \underline{\hspace{2cm}}$$

Using the data above for 50 °C and a mole fraction  $x_E = 0.6282$ , calculate the free energy and entropy of mixing for a one mole of a regular solution of iodoethane and ethyl acetate using the Raoult's law standard state activity. Compare the ideal free energy of mixing with non-ideal free energy of mixing.

Ideal

$$\Delta_{\text{mix}}G = \underline{\hspace{10em}}$$

$$\Delta_{\text{mix}}S = \underline{\hspace{10em}}$$

Non-ideal

$$\Delta_{\text{mix}}G = \underline{\hspace{10em}}$$

$$\Delta_{\text{mix}}S = \underline{\hspace{10em}}$$

3. Calculate the thermodynamic efficiency of an engine that runs at 430 K if the exhaust temperature is 310 K.

4. A. Given the expression

$$dU = TdS - PdV$$

Complete the following

$$dH = \underline{\hspace{10em}}$$

$$dG = \underline{\hspace{10em}}$$

$$dA = \underline{\hspace{10em}}$$

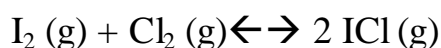
B. Derive an expression for the Maxwell relation for the total derivative of  $dA$ .

C. Use the Maxwell relation for  $dA$  to derive the Clausius-Clapeyron equation for the coexistence for curve of a liquid and vapor.

5. At 90 °C, the vapor pressure of toluene is 400 torr and that of o-xylene is 150 torr. What is the composition of the liquid when the liquid mixture boils at 90 °C when the pressure is 180 torr? What is the composition of the vapor produced?

6. The enthalpy of fusion of anthracene is 28.8 kJ/mol and its melting point is 217 °C. Calculate its ideal solubility in benzene.

7. Prior to the discovery that Freon-12 ( $\text{CF}_2\text{Cl}_2$ ) was harmful to the Earth's ozone layer, it was frequently used as the dispersing agent in spray cans for hair spray. Its enthalpy of vaporization at its normal boiling point of  $T_{\text{boil}} = -29.2\text{ }^\circ\text{C}$  is  $20.25\text{ kJ/mol}$ . Estimate the pressure that a can of hair spray using Freon-12 had to withstand at  $40\text{ }^\circ\text{C}$ , the temperature of a can that has been standing in sunlight. Assume that  $\Delta_{\text{vap}}H$  is a constant over the temperature range involved and equal to its value at  $-29.2\text{ }^\circ\text{C}$ .
8. The equilibrium constant for the reaction  $\text{I}_2(\text{s}) + \text{Br}_2(\text{g}) = 2\text{ IBr}(\text{g})$  is  $0.164$  at  $25\text{ }^\circ\text{C}$ . (a) Calculate  $\Delta_rG$  for this reaction (b) Bromine gas is introduced into a container with excess solid iodine. The pressure and temperature are held at  $0.164\text{ atm}$  and  $25\text{ }^\circ\text{C}$ . Find the partial pressure of  $\text{IBr}(\text{g})$  at equilibrium. (c) In fact, solid iodine has a vapor pressure of  $0.005\text{ atm}$  at  $25\text{ }^\circ\text{C}$ . Find the partial pressure of  $\text{IBr}(\text{g})$  accounting for the vapor pressure of iodine.
9. Calculate the entropy change when  $180\text{ grams}$  of boiling water are poured into a stainless steel bowl weighing  $110\text{ grams}$  at  $25\text{ }^\circ\text{C}$ . Assume that the molar mass of the metal in the bowl is  $55\text{ grams/mole}$ . The heat capacity of water is  $75\text{ J/mole-K}$  and that of bowl is  $25\text{ J/mole-K}$ .
11. Calculate the equilibrium constant for the reaction:



Use the molecular partition functions and the available data given below.

$$M(\text{Cl}) = 35.45\text{ a.u.}, M(\text{I}) = 126.9\text{ a.u.}$$

$$k_B = 0.697\text{ cm}^{-1}/\text{K} = 1.38 \times 10^{-23}\text{ J/K}$$

Note that rotational partition functions for homonuclear diatomics should include a symmetry number of 2.

Species	$h\nu\text{ (cm}^{-1}\text{)}$	$R_e\text{ (pm)}$	$D_e\text{ (kJ/mol)}$
$\text{I}_2$	204	266	151
$\text{Cl}_2$	534	199	243
$\text{ICl}$	380	234	104