

## 15.9: Problems

### Problems

Use data from the table below to find the thermodynamic properties requested in problems 1 to 7.

Properties	$CH_3OH$	$CH_3CH_2OH$
Density, $g\ cm^{-3}$ at 20 C	0.7914	0.7893
Mol mass, $g\ mol^{-1}$	32.04	46.07
bp, C	64.6	78.2
$\Delta_f G^\circ (300K, HIG^\circ) kJ\ mol^{-1}$	-159.436	-162.934
Vapor pressure at 320 K, bar	0.5063	0.2764
Virial coefficient, $B$ , $m^3\ mol^{-1}$	$-1.421 \times 10^{-3}$	$-2.710 \times 10^{-3}$

- Find the chemical potentials of the pure gases, assuming that they are ideal, taking the hypothetical ideal gas standard state as the standard state for activity ( $f = \tilde{a} = P$ ).
- Find the chemical potentials of the mixed gases, assuming that they are ideal, taking the hypothetical ideal gas standard state as the standard state for activity ( $f = \tilde{a}_A = x_A P$ ).
- Find the chemical potentials of the mixed gases, assuming them to obey the Virial equation,

$$PV/RT = 1 + (BP/RT),$$

assuming that the partial molar volumes in the mixture are equal to the partial molar volumes of the pure gases at the same pressure, and taking the hypothetical ideal gas standard state as the standard state for activity.

- Find the standard chemical potentials of the pure liquids at 320 K, assuming that the gases behave ideally.
- Find the standard chemical potentials of the pure liquids at 320 K, assuming that the gases obey the Virial equation.
- Find the chemical potential of the pure liquids as a function of pressure, assuming that the partial molar volumes of the pure liquids are constant and that the gases obey the Virial equation.
- Find the activity and chemical potential of the pure liquids at 101 bar, taking the pure liquids at 1 bar as the standard state for activity.
- A system is created by mixing one mole of gas  $A$  with one mole of gas  $C$ . Reaction occurs according to the stoichiometry  $A + C \rightleftharpoons D$ . Assume that the behaviors of these gases in their equilibrium mixture are adequately approximated by the Virial equations  $P\bar{V}_A/RT = 1 + (B_A P/RT)$ , etc.

(a) Show that the fugacity of gas A is given by

$$\ln f_A = \ln \left( \frac{x_A P}{P^\circ} \right) + \frac{B_A P}{RT}$$

(b) Write an equation for  $\mu_A = \mu_A(x_A, P)$  at constant temperature,  $T$ .

(c) Write an equation for  $\Delta_r \mu$ .

(d) Assume that

$\Delta_r \mu^\circ = \mu_D^\circ - \mu_A^\circ - \mu_C^\circ = 1000\ J\ mol^{-1}$ . If all three gases behave ideally ( $B_A = B_C = B_D = 0$ ), what is  $K_P$  for this reaction at 300 K? At equilibrium at 300 K and 1 bar, what are the mole fractions of  $A$ ,  $C$ , and  $D$ ?

(e) Under the assumptions in part (d), what are the equilibrium mole fractions of  $A$ ,  $C$ , and  $D$  at 300 K and 10 bar?

(f) Suppose that, contrary to the assumptions in (d) and (e), the Virial coefficients are not zero and that  $B_A = B_C = B_D = -10^{-3}\ m^3\ mol^{-1}$ . At equilibrium at 300 K and 1 bar, what are the mole fractions of  $A$ ,  $C$ , and  $D$ ?

(g) Under the assumptions in part (f), what are the equilibrium mole fractions of  $A$ ,  $C$ , and  $D$  at 300 K and 10 bar?

9. Suppose that the reaction  $A + C \rightleftharpoons D$  occurs in an inert solvent and that it is convenient to express concentrations as molarities. A frequently convenient choice of activity standard state for a solute is a hypothetical one-molar solution in which the chemical potential of the solute is equal to the chemical potential of the solute in a very ("infinitely") dilute solution in the same solvent. Then  $\tilde{a}_A = [A] \gamma_A$ , and  $\gamma_A \rightarrow 1$  as  $[A] \rightarrow 0$ . The thermodynamic equilibrium constant becomes

$$K_a = \frac{\tilde{a}_D}{\tilde{a}_A \tilde{a}_C} = \frac{[D]}{[A][C]} \frac{\gamma_D^d}{\gamma_A^a \gamma_C^c} = K_c K_\gamma$$

where we introduce

$$K_c = \frac{[D]}{[A][C]}$$

and

$$K_\gamma = \frac{\gamma_D^d}{\gamma_A^a \gamma_C^c}$$

In a very dilute solution,  $K_\gamma \rightarrow 1$  and  $K_c = K_a$ . Therefore, we can estimate  $K_a$  by finding the limiting value of  $K_c$  as all of the concentrations become very small. From values of  $K_c$  at higher concentrations, we can develop an empirical equation for  $K_\gamma$ . The form of this equation can be anything that can adequately represent the experimental data. Note, however, that finding an empirical model for  $K_\gamma$  does not solve the problem of finding empirical models for  $\gamma_A$ ,  $\gamma_C$ , and  $\gamma_D$  individually.

(a) Given that the hypothetical one-molar solution is chosen to be the activity standard state for all three species, what is the physical significance of  $\Delta_r \tilde{\mu}^o$ ?

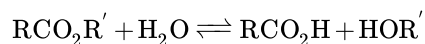
(b) A simple function that has the properties required of  $\gamma_A$  is  $\gamma_A = \alpha^{[A]}$ , where  $\alpha$  is a constant. Represent  $\gamma_C$  and  $\gamma_D$  by similar functions and show that this leads to  $\ln K_\gamma = \beta_A [A] + \beta_C [C] + \beta_D [D]$ , where  $\beta_A$ ,  $\beta_C$ , and  $\beta_D$  are constants.

(c) A series of solutions is prepared. The equilibrium concentrations of  $A$ ,  $B$ , and  $D$  in these solutions are given below. Calculate  $K_c$  for each solution. Estimate  $K_a$  and the parameters  $\beta_A$ ,  $\beta_C$ , and  $\beta_D$  in the equation of part (b).

[A]	[B]	[C]
$1.96 \times 10^{-3}$	$1.96 \times 10^{-3}$	$3.84 \times 10^{-5}$
$7.85 \times 10^{-3}$	$1.85 \times 10^{-3}$	$1.45 \times 10^{-4}$
$3.94 \times 10^{-2}$	$1.44 \times 10^{-3}$	$5.57 \times 10^{-4}$
$1.99 \times 10^{-1}$	$7.15 \times 10^{-4}$	$1.29 \times 10^{-3}$
$9.98 \times 10^{-1}$	$2.84 \times 10^{-4}$	$1.72 \times 10^{-3}$
$1.85 \times 10^{-3}$	$7.85 \times 10^{-3}$	$1.45 \times 10^{-4}$
$1.44 \times 10^{-3}$	$3.94 \times 10^{-2}$	$5.60 \times 10^{-4}$
$6.97 \times 10^{-4}$	$1.99 \times 10^{-1}$	$1.30 \times 10^{-3}$
$2.38 \times 10^{-4}$	$9.98 \times 10^{-1}$	$1.76 \times 10^{-3}$
$9.32 \times 10^{-3}$	$7.32 \times 10^{-3}$	$6.78 \times 10^{-4}$
$3.24 \times 10^{-2}$	$3.04 \times 10^{-2}$	$9.57 \times 10^{-3}$
$1.06 \times 10^{-1}$	$1.04 \times 10^{-1}$	$9.59 \times 10^{-2}$

(d) Using the values you find in part (c), estimate the equilibrium concentrations of  $A$ ,  $B$ , and  $D$  when a solution is prepared by mixing one mole of  $A$  with one mole of  $C$  and sufficient solvent to make 1 L of solution at equilibrium.

10. An ester,  $RCO_2R'$ , undergoes hydrolysis in an ether solvent:



We can express the activity of any of these species as the product of a concentration (in any convenient units) and an activity coefficient. When all of the reactants and products are present at low concentrations, the activity coefficients are approximately unity. The standard state for each species becomes a hypothetical solution of unit concentration in which the chemical potential (per mole) of that species is the same as its chemical potential in an arbitrarily (infinitely) dilute solution. A solution is prepared by mixing  $2 \times 10^{-3}$  mole of the ester and  $10^{-1}$  mole water in sufficient ether to make 1 L of solution. When equilibrium is reached, the acid and alcohol concentrations are  $9.66 \times 10^{-3}$  molar.

- (a) What is the equilibrium constant for this reaction?
- (b) A solution is prepared by mixing  $2 \times 10^{-2}$  mole of the acid,  $3 \times 10^{-2}$  mole of the alcohol, and  $10^{-1}$  mole of water in sufficient ether to make 1 L of solution. When equilibrium is reached, what is the concentration of the ester?
- (c) With this choice of the standard states, what physical process does the standard chemical-potential change,  $\Delta\tilde{\mu}^\circ$ , describe?

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