

Thermodynamics (Classical) for Biological Systems

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Additional Problems for Practice

The students have worked out many problems (tutorials), based on the principles discussed, during the class time itself, to improve understanding through active learning. The following problems are additional problems that the student can work out, to further strengthen the understanding of the course material, and to develop skills of application of the fundamentals. In addition, the students can work out the problems at the back of the relevant chapters in the text-book by Smith, VanNess and Abbott, given in the next Table.

Topic	Corresponding chapter in SVA
<i>Module 2: Additional useful thermodynamic functions</i>	
The thermodynamic functions H, A and G	6
Concept of chemical potential	10
Equations for a closed system, Maxwell's relations	6
Gibbs-Duhem equation	10
Thermodynamic analysis of processes – lost work, irreversibility	16
<i>Module 3: Thermodynamic properties of pure fluids</i>	
Review of ideal gas, non-ideal gas, fugacity, fugacity coefficient	10
PVT behaviour, virial and cubic equations of state, generalized correlations	3
Residual properties	6
Estimation of thermodynamic properties using equations of state	13
Estimation of the fugacity coefficient.	10
<i>Module 4: Thermodynamic properties of solutions</i>	
Ideal and non-ideal solutions, partial molar properties, excess properties of mixtures, activity coefficient and its estimation.	10
<i>Module 5: Phase Equilibria</i>	
Criteria for phase equilibria	10
Phase rule	2
Clausius-Clayperon equation	6
VLE for pure component, VLE for multi-component system	11
<i>Module 6: Reaction Equilibria</i>	
Equilibrium criteria for homogenous reactions, evaluation of equilibrium constant, effect of temperature and pressure on equilibrium constant	15
Ionic equilibria	None

1. At high temperature, 1 mole of a non-ideal gas in a system undergoes changes isothermally. A PV versus P curve is drawn for that. Using the Van der Waals EOS

(i) Find RT at minima of the curve

(ii) Find T given that at minima $P = 0$ (approx)

(problem formulated by Pallavi Singh)

2. Show that $C_p - C_v = TV \frac{\alpha^2}{\kappa}$

3. Show that (derive) the constants in the Redlich-Kwong equation of state can be expressed in terms of the critical properties as

$$a = \frac{0.42748 R^2 T_c^{2.5}}{P_c} \quad b = \frac{0.08664 R T_c}{P_c}$$

4. For a pure bio-substance, the compressibility factor was given by the first three terms of the virial expansion in terms of the pressure, i.e. $Z = 1 + B_1 P + B_2 P^2$. Express the following quantities for such a bio-substance in terms of P , T , B_1 and B_2 alone: (a) fugacity coefficient (b) fugacity (c) G^R (d) V^R (e) H^R

(problem formulated by Akhil Sai Valluri)

5. A solution mixture is made up of methanol and ethanol. The difference in volume of the solutions upon mixing is given by $\Delta V = 4 x_2 + 24$, where x_2 is the mole fraction of ethanol. If the initial volume of ethanol taken was 10 L, then estimate the partial molar volume of ethanol solution in the given mixture.

(problem formulated by Pallavi Chakraborty and V. Sowmya)

6. A solution of an imaginary liquid and water is prepared. 0.2 moles of the liquid is again added to the solution prepared, and mixed thoroughly, to retain the same temperature $T = 300$ K, and pressure $P = 0.5$ bar. For this liquid, γ , i.e., the activity co-efficient, is found to be a function of pressure, and is known to be $\gamma = \exp(P^4 + 0.5 P^2)$. The calculated molar volume (ideal) of the

imaginary liquid is $1260 \text{ m}^3 \text{ mol}^{-1}$. Find the change in the volume of the solution on addition of the excess liquid.

(problem formulated by Chetan Shenoy and Kanishka Waghmare)

7. Ampicillin is a β -lactam antibiotic that has been extensively used to treat bacterial infections. It is able to penetrate gram +ve and some gram -ve bacterial cell envelopes. An ampicillin solution in distilled water has a molar volume (in $\text{m}^3 \text{ mol}^{-1}$) given by the following equation, in terms of the relevant mole fractions; the subscript 1 refers to ampicillin:

$$V = 5x_1 + 30x_2 + 15x_1x_2$$

Find the expressions for the partial molar volumes of ampicillin and water. Also find the expressions for the partial molar volumes at infinite dilution.

(problem formulated by Shikha Jain)

8. Consider the reaction of splitting water into oxygen and hydrogen (where does splitting water occur in nature?). Find the number of degrees of freedom for this system.

(problem formulated by Akhil Sai Valluri and Aman Kumar)

9. Starting with Eq. 6.27 (discussed in the class), and by following a similar procedure to arrive at the Van't Hoff's equation, derive Eq. 6.41.

10. Starting with Eq. 6.47 (discussed in the class), derive Eq. 6.48