## CHEM 2011.03

## **Introduction to Thermodynamics**

- Know the difference between macroscopic and microscopic quantities.
- Understand that thermodynamics deals with macroscopic quantities.
- Be able to use the concept of equilibrium.
- Know and be able to use the ideal gas law: PV = nRT.
- Know that the ideal gas temperature scale is the correct thermodynamic temperature scale.
- Know that temperature is a measure of thermal kinetic energy and that *RT* provides the scale for thermal energy.
- Understand what internal energy consists of and how heat, internal energy, and temperature differ from one another.
- Be able to state and apply the First Law of Thermodynamics in terms of heat and work:  $\Delta U = q + w$ .
- Know what is meant by a reversible process.
- Be familiar with the terms "system" and "surroundings".
- Understand the distinction between state functions and path functions. Know that only a small number of state functions are needed to fully specify the state of a system.
- Know and be able to use the definition of *PV* work.
- Know and be able to use the definition of enthalpy: H = U + PV.
- Be able to calculate heat, work,  $\Delta U$ , and  $\Delta H$  for isothermal and constant pressure processes.
- Know that for an ideal gas, *H* and *U* depend on temperature alone; but this is not true for other substances.
- Know when  $\Delta U$  or  $\Delta H$  can be equated to q. Know the definitions of  $C_{\rm v}$  and  $C_{\rm p}$  in terms of U and H. Be able to use  $C_{\rm v}$  and  $C_{\rm p}$  in calculations involving the transfer of energy as heat.
- Understand the terms isothermal, adiabatic, and diathermic.
- Know the definition of entropy:  $dS = dq_{rev} / T$ . Be able to use it and the fact that entropy is a state function to calculate entropy changes.
- Be able to give Clausius's statement of the Second Law of Thermodynamics. Understand the significance of the entropy change of the universe as opposed to the entropy change of the system.
- Know that increases in *T* produce increases in *U*, *H*, and *S*; but *U*, *H*, and *S* can change with no change in *T*. Understand why this is so.

- Be able to predict the sign of the entropy change in phase transitions, heating and cooling, and processes involving the change in pressure or volume of gases.
- Know what is meant by cyclic, reversible, spontaneous, and isentropic processes and be able to calculate entropy changes in such processes.
- Understand that heat engines use the transfer of heat between two different temperatures to do work and that there is a fundamental limit to the efficiency of such engines.
- Know that it is impossible to devise a process that has the sole effect of turning heat into work.
- Understand that the quality of an energy source depends on the amount of entropy associated with a transfer of energy from the source.
- Be able to take partial derivatives of a function of several variables.
- Be able to write out the total differential of a function of several variables.
- Be able to use the definitions of H, A, and G. These will be provided on the test.
- Be able to write out the fundamental equation of thermodynamics (dU = TdS PdV) in terms of U, H, A, and G for closed systems of fixed composition.
- Know which of T, S, P and V are the "natural variables" for each of U, H, A, and G.
- Be able to correctly carry out the basic partial derivative manipulations: Maxwell relations (equivalence of mixed second derivatives), inverses, chain rule, cyclic rule, and rearrangements of the fundamental equation.
- Be able to use numerical values of partial derivatives to estimate the change in one quantity from the change in another, such using  $C_v$  to estimate the change in U due to a change in T at constant V or using  $\beta$  to estimate the change in V when P changes at constant T.
- Know that Gibbs free energy gives the direction of spontaneous change for a process at constant temperature and pressure and understand why that is so.
- Know the definition of partial molar quantities. Know that they are equivalent to molar quantities for pure substances.
- Know that the Third Law of Thermodynamics postulates that the entropy of a perfect crystal is zero at the absolute zero of temperature. Understand that this can be used to compute absolute entropies.
- Understand that entropy increases with: increasing *T*, changing a low *T* phase to a higher *T* phase, increasing the molecular weight and/or complexity of molecules, and when a chemical reaction increases the number of moles of gas.
- Be able to define standard states and standard enthalpy and entropy changes; understand what is meant by reference states.

- Be able to calculate  $\Delta S^{\circ}_{rxn}$ ,  $\Delta G^{\circ}_{P,rxn}$ ,  $\Delta C^{\circ}_{P,rxn}$ , and  $\Delta H^{\circ}_{rxn}$  from tabulated data.
- Understand how to use  $\Delta C^{\circ}_{P,rxn}$  to compute the temperature dependencies of  $\Delta H^{\circ}_{rxn}$  and  $\Delta S^{\circ}_{rxn}$ .
- Know how to use  $\Delta G = \Delta H T\Delta S$  to estimate  $\Delta G^{\circ}_{rxn}$  at a temperature other than that for which the data are tabulated.
- Understand which tabulated thermodynamic quantities are for formation of the species (and be able to give the corresponding reaction) and which are absolute quantities.
- Understand that  $\Delta S_{rxn}$  and  $\Delta G_{rxn}$  are sensitive to pressure if gases are involved in the reaction.
- Be able to determine the number of phases and components from a description of a system.
- Know that the chemical potential is the partial molar Gibbs free energy.
- Know that at equilibrium the chemical potential of a substance must be the same in all phases.
- Know and be able to use the Gibbs phase rule: f = 2 + c p.
- Know that higher temperature favors the higher entropy phase and higher pressure favors the higher density phase.
- Know what is meant by a metastable phase.
- Be able to sketch a single component phase diagram; be able to label the various regions, the triple point, and the critical point; and be able to describe what happens as a particular path is followed on the phase diagram.
- Be able to use the the Clapeyron equation and the equations for the temperature and pressure dependence of the chemical potential. These equations will be provided if needed:

$$\frac{dP}{dT} = \frac{\Delta H_{tr}}{T\Delta V_{tr}} \qquad \left(\frac{\partial \mu_i}{\partial T}\right)_P = -\overline{S}_i \qquad \left(\frac{\partial \mu_i}{\partial P}\right)_T = \overline{V}_i$$

- Know the Clausius-Clapeyron equation: Know when it is applicable and be able to use it.
- Know the relation between chemical potential and activity:  $\mu_i = \mu_i^{\circ} + RT \ln a_i$ .
- Know the common approximations for activity for solids, liquids, gases, and species in solution.

 $\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_{vap}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$ 

- Know the difference between  $\Delta G_{rxn}$  and  $\Delta G^{\circ}_{rxn}$ . Know what each is used for and know that  $\Delta G_{rxn} = 0$  at equilibrium.
- Know and be able to use the Lewis equation together with the definitions of activity quotient and equilibrium constant:  $\Delta G_{rxn} = \Delta G^{\circ}_{rxn} + RT \ln Q$  and  $\Delta G^{\circ}_{rxn} = -RT \ln K_{eq}$ .

- Understand why equilibrium might never be reached if there is only one degree of freedom.
- Know and be able to use the van't Hoff equation:  $\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta H^{\circ}_{rxn}}{R} \left(\frac{1}{T_1} \frac{1}{T_2}\right).$
- Understand and be able to use LeChatelier's principle.
- Know the properties of ideal solutions ( $\Delta H_{\text{mix}} = 0$ ,  $\Delta V_{\text{mix}} = 0$ , Raoult's Law). Understand the physical reason for deviations from ideal solution behavior.
- Be able to calculate the Gibbs free energy of mixing, for ideal and non-ideal solutions, starting from pure substances:  $\Delta G_{mix} = nRT \sum_{i} X_i \ln a_i$ .
- Understand that for ideal systems the Gibbs free energy of mixing is entirely due to entropy.
- Be able to calculate the composition of the vapor phase in equilibrium with a solution. Know that for equilibrium with ideal solutions the vapor phase is always enriched in the more volatile component.
- Understand and be able to use Henry's Law in terms of both mole fraction and molality.
- Know how to convert between mole fraction and molality. Know that for aqueous solutions molar concentration is approximately equal to molality.
- Know and be able to use the definitions of activity and, when appropriate, activity coefficients for the various common standard states: pure solid, pure liquid, ideal gas, solvent, solute using the mole fraction scale, and solute using the molal scale.
- Understand that the Gibbs-Duhem equation may be used to calculate the activity of one component from the activities of other components.
- Understand that thermodynamic properties can not be determined for individual ions and that, by convention,  $\Delta H^{\circ}_{f}$ ,  $\Delta G^{\circ}_{f}$ , and  $\overline{S}^{\circ}$  are set to zero for the hydrogen ion.
- Know how to use the mean ionic activity coefficient in equilibrium expressions, how to calculate the ionic strength of an electrolyte solution, and how to use the Debye-Huckel equation to calculate mean ionic activity coefficients. If needed, the following equations will be provided:

$$a_{\pm} = \gamma_{\pm} m_{\pm}$$
  $I = \frac{m}{2} \sum_{i} v_{i} Z_{i}^{2}$   $\ln \gamma_{\pm} = -\frac{1.173 |\mathbf{Z}_{+} \mathbf{Z}_{-}| \sqrt{I}}{1 + \sqrt{I}}$ 

• Know and be able to use the Nernst equation and the relationship between cell potential and free energy of reaction:  $E = E^{\circ} - \frac{RT}{vF} \ln Q$  and  $\Delta G^{\circ}_{rxn} = -vFE$ . This includes knowing how to determine the number of moles of electrons transferred, v.