

# INTERMEDIATE CHEMISTRY

## TERMINOLOGY OF CHEMICAL THERMODYNAMICS

**Adiabatic process:** Process in which no heat is exchanged between system and surroundings (such as an insulated reaction vessel where  $q = 0$ )

**Bond dissociation energy,  $\Delta H_f^\circ$ :** Enthalpy change required to break a specific bond between two atoms in the gaseous state

**Calorimeter:** A device that measures heat

**Endothermic process:** Process in which the system absorbs heat

**Enthalpy,  $H$ :** A thermodynamic quantity to describe heat transferred between system and surroundings at constant pressure (sometimes referred to as heat content)

**Enthalpy of reaction,  $\Delta H_r^\circ$ :** The difference between the enthalpies of products and reactants

**Entropy,  $S$ :** A thermodynamic property which is a direct measure of randomness or disorder of a system

**Exothermic process:** Process in which a system gives off heat to its surroundings

**First law of thermodynamics:** Energy can be converted from one form to another, but cannot be created or destroyed

**Free energy,  $G$ :** A property measuring the energy to do useful work

**Heat,  $q$ :** Energy transferred between two bodies at different temperatures, calculated as mass  $\times$  heat capacity  $\times$  temperature change of a body

[that is,  $q = m(c_p \Delta T) = (m \times c_p) \times (T_{\text{final}} - T_{\text{initial}})$ ]

**Heat capacity,  $C$ :** Heat required to raise the temperature of a given amount of substance by one degree Celsius or Kelvin (such as  $C_{\text{water}} = 4.18 \text{ J/g}^\circ\text{C} = 75.3 \text{ J/mol}^\circ\text{C}$ )

**Heat flow:** The change in enthalpy in a reaction in the sense whether the reaction takes place in one step or a series of steps

**Internal energy,  $U$ :** The total sum of kinetic, vibrational, and rotational energy of molecules

**Isochoric process:** A process carried out at constant pressure (such as reaction in an open vessel exposed to a constant pressure atmosphere)

**Isochoric process:** Process carried out at constant volume (such as heating of a gas in a closed container)

**Isothermal process:** Process carried out at constant temperature (such as reaction vessel immersed in a constant temperature bath)

**Latent heat of fusion,  $\Delta H_f^\circ$ :** Heat required to convert a unit mass of solid to liquid at constant temperature (such as for  $\text{H}_2\text{O}$ ,  $\Delta H_f^\circ = 334 \text{ J/g} = 6.01 \text{ kJ/mol}$ )

**Latent heat of vaporization,  $\Delta H_v^\circ$ :** Heat required to convert a unit mass of liquid to vapor at constant temperature (such as for  $\text{H}_2\text{O}$ ,  $\Delta H_v^\circ = 2.27 \text{ kJ/g} = 40.8 \text{ kJ/mol}$ )

**Second law of thermodynamics:** The entropy of a system and its surroundings increases in a spontaneous process and remains unchanged in an equilibrium process; for a spontaneous process, either  $\Delta S$ , or  $\Delta S_{\text{univ}}$  may be negative, but the sum must be positive ( $\Delta S_{\text{univ}} > 0$ )

**Standard enthalpy of formation,  $\Delta H_f^\circ$ :** Enthalpy change at constant pressure when one mole of a compound is formed from its elements at  $25^\circ\text{C}$  and 1 atmosphere

**Standard enthalpy of reaction,  $\Delta H_r^\circ$ :** Enthalpy change when a reaction is carried out at  $25^\circ\text{C}$  and 1 atmosphere (atm)

**State functions:** System property determined only by initial and final states and not on the intermediate transition path • Some examples are:  $T$ ,  $P$ ,  $H$ ,  $S$ ,  $G$  • Heat ( $q$ ) and work ( $w$ ) are not state functions since they are energy losses in transition between system and surroundings (that is, non-state functions are path dependent)

**Surroundings:** Domain outside the system being considered (such as atmosphere surrounding a vessel)

**System:** A specific entity with clearly defined boundaries containing substance, or vessel in which a reaction takes place, or a piston and cylinder in which a gas expands or contracts

**Thermodynamics:** The study of thermal energy changes (such as changes in  $q$  and  $U$  in exothermic and endothermic reactions)

**Thermodynamics:** The study of the interconversion of various energy forms: chemical, mechanical, chemical, electrical

**Work,  $w$ :** Energy transfer between system and surroundings resulting from a force  $F$  acting over a distance  $\Delta x$  ( $w = F \Delta x$ ) or a pressure  $P$  associated with a volume change  $\Delta V$  ( $w = P \Delta V$ )

## FIRST LAW OF THERMODYNAMICS

• A statement of conservation of energy • Energy cannot be created or destroyed; it can only be transformed into other forms

$$\Delta E_{\text{sys}} = E_{\text{surround}} + \Delta q + \Delta w$$

Change in internal energy of system	Heat absorbed from surroundings	Work done by surroundings
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Special Cases

$q = 0$  Adiabatic process

$w = 0$  Isochoric process  
Heat exchanged at constant volume

### EXAMPLE

- Work done in the compression of a gas in a cylinder is  $44.2 \text{ J}$  • At the same time, the temperature rises and  $1.18 \text{ J}$  of heat is transferred to the surroundings
- Calculate the change in energy of the system
- $\Delta w$  done on system is positive, heat given off to surroundings is negative (see Sign Rules) • Hence  $\Delta E = q + w = -1.18 \text{ J} + 44.2 \text{ J} = 43.0 \text{ J}$
- The compression work done on the system outweighs the heat lost to the surroundings and there is a net increase in the internal energy of the system of  $43.0 \text{ J}$

## ENTROPY, $S$

- $S$  is a direct measure of randomness and disorder of a system
- It increases when a substance (S) melts (M) vaporizes (V) dissolves (D) is heated
- It equals  $\Delta S/T$  at equilibrium

### ABSOLUTE ENTROPY, $S^\circ$ (25°C, 1 atm)

Substance	$S^\circ$ (J/K-mol)	Substance	$S^\circ$ (J/K-mol)
Oxygen	205	Ethane	229
Hydrogen	131	Ethylene	220
Graphite	5.69	Acetylene	200
Water (l)	69.9	Benzene (l)	125
Water (s)	37	Methanol (l)	127
Carbon dioxide	214	Ethanol (l)	160
Methane	188	Glucose (s)	212

### EXAMPLE

- Use tabulated values of  $\Delta H_f^\circ$  and  $\Delta S_f^\circ$  to calculate  $\Delta G_{\text{vap}}$  and  $\Delta G_{\text{liq}}$  for benzene

$$\begin{aligned} \text{Solvent } \Delta G_{\text{vap}} &= \frac{\Delta H_{\text{vap}}}{T_{\text{vap}}} - \frac{T_{\text{vap}} \Delta S_{\text{vap}}}{T_{\text{vap}}} \\ &= 30.9 \text{ J/mol-K} \end{aligned}$$

$$\begin{aligned} \text{Evaporation } \Delta G_{\text{liq}} &= \frac{\Delta H_{\text{liq}}}{T_{\text{liq}}} - \frac{T_{\text{liq}} \Delta S_{\text{liq}}}{T_{\text{liq}}} \\ &= -87.83 \text{ J/mol-K} \end{aligned}$$

- In both cases  $\Delta S > 0$  because of the greater disorder caused by each process •  $\Delta S_{\text{liq}} > \Delta S_{\text{vap}}$  since evaporation creates more disorder than the melting process

# Chemistry Study Guide 4

**Anthony S. Fauci**



## Chemistry Study Guide 4 :

*Organic Chemistry, 12e Binder Ready Version Study Guide & Student Solutions Manual* T. W. Graham Solomons, Craig B. Fryhle, Scott A. Snyder, 2016-04-11 This is the Student Study Guide Solutions Manual to accompany Organic Chemistry 12th Edition The 12th edition of Organic Chemistry continues Solomons Fryhle Snyder s tradition of excellence in teaching and preparing students for success in the organic classroom and beyond A central theme of the authors approach to organic chemistry is to emphasize the relationship between structure and reactivity To accomplish this the content is organized in a way that combines the most useful features of a functional group approach with one largely based on reaction mechanisms The authors philosophy is to emphasize mechanisms and their common aspects as often as possible and at the same time use the unifying features of functional groups as the basis for most chapters The structural aspects of the authors approach show students what organic chemistry is Mechanistic aspects of their approach show students how it works And wherever an opportunity arises the authors show students what it does in living systems and the physical world around us

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