Chemistry 132 NT

It takes a big man to cry, but it takes a bigger man to laugh at that man.

Jack Handey

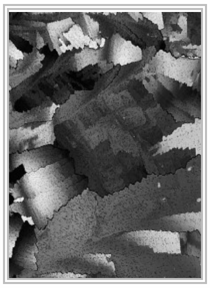
Chem 132 NT

Thermodynamics and Equilibrium

Module 1

Spontaneous Processes and Entropy

- **First Law of Thermodynamics: Enthalpy**
- **Entropy and the Second Law of Thermodynamics**
- **Standard Entropies and the Third Law of Thermodynamics**



Photomicrograph of urea crystals under polarized light.

Thermodynamics

- **Thermodynamics** is the study of the relationship between heat and other forms of energy in a chemical or physical process.
  - We introduced the thermodynamic property of **enthalpy, H,** in first-semester chemistry.
  - We noted that the **change in enthalpy equals the heat of reaction at constant pressure**.
  - In this chapter we will define enthalpy more precisely, in terms of the energy of the system.

First Law of Thermodynamics

- To state the **laws of thermodynamics**, we must first understand the internal energy of a system and how you can change it.
  - The **internal energy, U**, is the sum of the kinetic and potential energies of the particles making up the system.
  - Internal energy is a **state function**. That is, a property of a system that depends only on its present state.

First Law of Thermodynamics

- To state the **laws of thermodynamics**, we must first understand the internal energy of a system and how you can change it.
  - Thus, 1 mol of water at 0 °C and 1 atm pressure has a definite quantity of energy.
  - When a system changes from one state to another, its internal energy changes.

$$D\mathbf{U} = \mathbf{U}_{\mathbf{final}} - \mathbf{U}_{\mathbf{initial}}$$

First Law of Thermodynamics

- To state the **laws of thermodynamics**, we must first understand the internal energy of a system and how you can change it.
  - Changes in U manifest themselves as **exchanges of energy** between the system and surroundings.
  - These exchanges of energy are of two kinds; **heat** and **work**.

First Law of Thermodynamics

- To state the **laws of thermodynamics**, we must first understand the internal energy of a system and how you can change it.
  - **Heat** is energy that moves into or out of a system because of a **temperature difference** between system and surroundings.
  - **Work**, on the other hand, is the energy exchange that results when a **force F** moves an object through a **distance d**; **work (w) = F´ d**

First Law of Thermodynamics

- To state the **laws of thermodynamics**, we must first understand the internal energy of a system and how you can change it.
  - Remembering our sign convention.

    Work done by the system is **negative**.

    Work done on the system is **positive**.

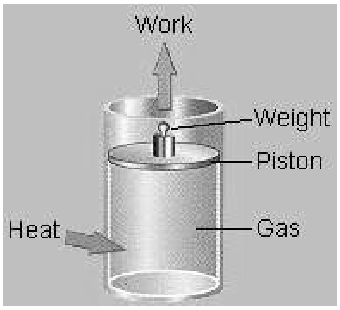
    Heat evolved by the system is **negative**.

    Heat absorbed by the system is **positive**.

First Law of Thermodynamics

- To state the **laws of thermodynamics**, we must first understand the internal energy of a system and how you can change it.
  - The figure on the next slide illustrates the distinction between heat and work.
  - The system in this figure gains internal energy from the heat absorbed and loses internal energy via the work done.

Exchanges of heat and work with the surroundings



A gas is enclosed in a vessel with a piston. Heat flows into the vessel from the surroundings., which are at a higher temperature. As the temperature of the gas increases, the gas expands, lifting the weight (doing work).

First Law of Thermodynamics

- To state the **laws of thermodynamics**, we must first understand the internal energy of a system and how you can change it.
  - In general, the **first law of thermodynamics** states that the change in internal energy, ΔU , equals heat plus work.

$$D\mathbf{U} = \mathbf{q} + \mathbf{w}$$

Heat of Reaction and Internal Energy

- When a reaction is run **in an open vessel** (at constant P), any gases produced represent a potential source of **“expansion” work**.
  - When gases are produced, they exert **force** on the surroundings as pressure.
  - If the reaction is run at constant pressure, then the gases produced represent a change in volume analogous to a **distance** over which a force is exerted.

Heat of Reaction and Internal Energy

- When a reaction is run **in an open vessel** (at constant P), any gases produced represent a potential source of **“expansion” work**.
  - It follows therefore, that

$$w = -P\Delta V$$

  - You can calculate the work done by a chemical reaction simply by multiplying the atmospheric pressure by the change in volume, ΔV.

Heat of Reaction and Internal Energy

- When a reaction is run **in an open vessel** (at constant P), any gases produced represent a potential source of **“expansion” work**.
  - For example, when 1.00 mol Zn reacts with excess HCl, 1.00 mol H_2 is produced.

$$Zn(s) + 2H_3O^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g) \qquad q_p = -152.4\ kJ$$

Heat of Reaction and Internal Energy

- When a reaction is run **in an open vessel** (at constant P), any gases produced represent a potential source of **“expansion” work**.
  - At 25 °C and 1.00 atm (1.01×10^5 Pa), this amount of H_2 occupies 24.5 L ($24.5 \times 10^{-3} m^3$).

$$Zn(s) + 2H_3O^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g) \qquad q_p = -152.4\ kJ$$

Heat of Reaction and Internal Energy

- When a reaction is run **in an open vessel** (at constant P), any gases produced represent a potential source of **“expansion” work**.
  - The work done by the chemical system in pushing back the atmosphere is

$$\mathbf{w} = -P\Delta V = -(1.01 \times 10^5\,\mathrm{Pa}) \times (24.5 \times 10^{-3}\,\mathrm{m}^3)$$
$$= -2.47 \times 10^3\,\mathrm{J} \text{ or } -2.47\,\mathrm{kJ}$$

Heat of Reaction and Internal Energy

- When a reaction is run **in an open vessel** (at constant P), any gases produced represent a potential source of **“expansion” work**.
  - Relating the change in internal energy to the heat of reaction, you have

$$\Delta U = q_p + w$$
$$\Delta U = (-152.4\,\mathrm{kJ}) + (-2.47\,\mathrm{kJ})$$
$$\Delta U = -154.9\,\mathrm{kJ}$$

Heat of Reaction and Internal Energy

- When a reaction is run **in an open vessel** (at constant P), any gases produced represent a potential source of **“expansion” work**.
  - When the reaction occurs, the internal energy changes as the kinetic and potential energies change in going from reactants to products.
  - Energy leaves the system **mostly as heat** (q_p = -152.4 kJ) but **partly as expansion work** (-2.47 kJ).

Enthalpy and Enthalpy Change

- In first-semester chemistry, we tentatively defined enthalpy in terms of the relationship of Δ**H** to the **heat at constant pressure**.
  - We now define **enthalpy, H**, precisely as the quantity (U – w) or U – (–PΔV).
  - Because U, P, and V are state functions, H is also a state function.

Enthalpy and Enthalpy Change

- In first-semester chemistry, we tentatively defined enthalpy in terms of the relationship of Δ**H** to the **heat at constant pressure**.
  - This means that at a given temperature and pressure, a given amount of a substance has a definite enthalpy.
  - Therefore, **if you know the enthalpies of substances, you can calculate the change in enthalpy, ΔH, for a reaction.**

Enthalpy and Enthalpy Change

- In first-semester chemistry, we tentatively defined enthalpy in terms of the relationship of Δ**H** to the **heat at constant pressure**.
  - In practice, we measure certain heats of reactions and use them to tabulate enthalpies of formation, ΔH^{o}_{f}.
  - Standard enthalpies of formation for selected compounds are listed in the appendix of your text.

Enthalpy and Enthalpy Change

- In first-semester chemistry, we tentatively defined enthalpy in terms of the relationship of ΔH to the **heat at constant pressure**.
  - The standard enthalpy change for a reaction is

$$\Delta H^{o} = \sum n\Delta H_{f}^{o}(\text{products}) - \sum m\Delta H_{f}^{o}(\text{reactants})$$

Spontaneous Processes and Entropy

- A **spontaneous process** is a physical or chemical change that occurs by itself.
  - Examples include:
    - A rock at the top of a hill rolls down.
    - Heat flows from a hot object to a cold one.
    - An iron object rusts in moist air.
  - These processes occur without requiring an outside force and **continue until equilibrium is reached**.

Entropy and the Second Law of Thermodynamics

- The **second law of thermodynamics** addresses questions about spontaneity in terms of a quantity called **entropy**.
  - **Entropy, S**, is a thermodynamic quantity that is a measure of the randomness or disorder of a system.
  - The SI unit of entropy is **joules per Kelvin (J/K)** and, like enthalpy, is a state function.

Entropy and the Second Law of Thermodynamics

- The **second law of thermodynamics** states that the total entropy of a system and its surroundings always increases for a spontaneous process.
  - The net change in entropy of the system, ΔS , equals the sum of the entropy created during the spontaneous process and the change in energy associated with the heat flow.

Entropy and the Second Law of Thermodynamics

- The **second law of thermodynamics** states that the total entropy of a system and its surroundings always increases for a spontaneous process.
  - In other words,

$$\Delta S = \textbf{entropy created} + \frac{q}{T}$$

(For a spontaneous process)

Entropy and the Second Law of Thermodynamics

- The **second law of thermodynamics** states that the total entropy of a system and its surroundings always increases for a spontaneous process.
  - Normally, the quantity of entropy created during a spontaneous process cannot be directly measured.

Entropy and the Second Law of Thermodynamics

- The **second law of thermodynamics** states that the total entropy of a system and its surroundings always increases for a spontaneous process.
  - If we delete it from our equation, we can conclude

$$DS > \frac{q}{T}$$

(For a spontaneous process)

Entropy and the Second Law of Thermodynamics

- The **second law of thermodynamics** states that the total entropy of a system and its surroundings always increases for a spontaneous process.
  - The restatement of the second law is as follows: **for a spontaneous process, the change in entropy of the system is greater than the heat divided by the absolute temperature.**

Entropy Change for a Phase Transition

- If during a **phase transition**, such as ice melting, heat is slowly absorbed by the system, it remains near equilibrium as the ice melts.
  - Under these conditions, no significant amount of entropy is created.
  - The entropy results entirely from the absorption of heat. Therefore,

$$DS = \frac{q}{T}$$

(For an equilibrium process)

Entropy Change for a Phase Transition

- If during a **phase transition**, such as ice melting, heat is slowly absorbed by the system, it remains near equilibrium as the ice melts.
  - Other phase changes, such as vaporization of a liquid, also occur under equilibrium conditions.
  - Therefore, you can use the previous equation to obtain the entropy change for a phase change.

A Problem To Consider

- The heat of vaporization, ΔH_{vap} of carbon tetrachloride, CCl_4, at 25 ^oC is 43.0 kJ/mol. If 1 mol of liquid CCl_4 has an entropy of 214 J/K, **what is the entropy of 1 mol of the vapor** at this temperature?
  - When liquid CCl_4 evaporates, it absorbs heat: ΔH_{vap} = 43.0 kJ/mol (43.0 x 10^3 J/mol) at 25 ^oC, or 298 K. The entropy change, ΔS, is

$$\Delta S = \frac{\Delta H_{vap}}{T} = \frac{\mathbf{43.0 \times 10^3 J/mol}}{\mathbf{298K}} = \mathbf{144\,J/(mol \cdot K)}$$

A Problem To Consider

- The heat of vaporization, ΔH_{vap} of carbon tetrachloride, CCl_4, at 25 ^oC is 43.0 kJ/mol. If 1 mol of liquid CCl_4 has an entropy of 214 J/K, **what is the entropy of 1 mol of the vapor** at this temperature?
  - In other words, 1 mol of CCl_4 increases in entropy by 144 J/K when it vaporizes.
  - The entropy of 1 mol of vapor equals the entropy of 1 mol of liquid (214 J/K) plus 144 J/K.

$$\textbf{Entropy of vapor} = \mathbf{(214 + 144) J/K = 358\,J/K}$$

Entropy, Enthalpy, and Spontaneity

- Now you can see how thermodynamics is applied to the question of **reaction spontaneity**.
  - Recall that the heat at constant pressure, q_p , equals the enthalpy change, ΔH.
  - The second law for a spontaneous reaction at constant temperature and pressure becomes

$$DS > \frac{q_p}{T} = \frac{DH}{T}$$ **(Spontaneous reaction, constant T and P)**

Entropy, Enthalpy, and Spontaneity

- Now you can see how thermodynamics is applied to the question of **reaction spontaneity**.
  - Rearranging this equation, we find

$$DH - TDS < 0$$ **(Spontaneous reaction, constant T and P)**

  - This inequality implies that for a reaction to be spontaneous, D**H-T**D**S must be negative**.
  - If ΔH-TΔS is positive, the reverse reaction is spontaneous. If ΔH-TΔS=0, the reaction is at equilibrium.

Standard Entropies and the Third Law of Thermodynamics

- The **third law of thermodynamics** states that a substance that is perfectly crystalline at 0 K has an entropy of zero.
  - When temperature is raised, however, the substance becomes more disordered as it absorbs heat.
  - The entropy of a substance is determined by measuring how much heat is required to change its temperature per Kelvin degree.

Standard Entropies and the Third Law of Thermodynamics

- The **standard entropy** of a substance or ion, also called its **absolute entropy, S°**, is the entropy value for the standard state of the species.
  - Standard state implies 25 °C, 1 atm pressure, and 1 M for dissolved substances.

Standard Entropies and the Third Law of Thermodynamics

- The **standard entropy** of a substance or ion, also called its **absolute entropy, S°**, is the entropy value for the standard state of the species.

  - Note that the **elements have nonzero values**, unlike standard enthalpies of formation, ΔH_f^o , which by convention, are zero.

Standard Entropies and the Third Law of Thermodynamics

- The **standard entropy** of a substance or ion, also called its **absolute entropy, S°**, is the entropy value for the standard state of the species.

  - The symbol S^o, rather than ΔS^o, is used for standard entropies to emphasize that they originate from the third law.

Entropy Change for a Reaction

- You can **calculate the entropy change** for a reaction using a summation law, similar to the way you obtained ΔH^o.

$$\Delta S^o = \sum n\Delta S^o(\text{products}) - \sum m\Delta S^o(\text{reactants})$$

  - Even without knowing the values for the entropies of substances, you can sometimes predict the sign of ΔS^o for a reaction.

Entropy Change for a Reaction

- You can **calculate the entropy change** for a reaction using a summation law, similar to the way you obtained ΔH^o.
  - The entropy usually increases in the following situations:
    1. A reaction in which a molecule is broken into two or more smaller molecules.

Entropy Change for a Reaction

- You can **calculate the entropy change** for a reaction using a summation law, similar to the way you obtained ΔH^o.
  - The entropy usually increases in the following situations:
    2. A reaction in which there is an increase in the moles of gases.

Entropy Change for a Reaction

- You can **calculate the entropy change** for a reaction using a summation law, similar to the way you obtained ΔH^o.
  - The entropy usually increases in the following situations:
    3. A process in which a solid changes to liquid or gas or a liquid changes to gas.

A Problem To Consider

- Calculate the change in entropy, ΔS^o, at 25 ^oC for the reaction in which urea is formed from NH_3 and CO_2. The standard entropy of NH_2CONH_2 is 174 J/(molK). See the appendix in your text for other values.

$$2NH_3(g) + CO_2(g) \rightarrow NH_2CONH_2(aq) + H_2O(l)$$

  - The calculation is similar to that used to obtain ΔH^o from standard enthalpies of formation.

A Problem To Consider

- Calculate the change in entropy, ΔS^o, at 25 ^oC for the reaction in which urea is formed from NH_3 and CO_2. The standard entropy of NH_2CONH_2 is 174 J/(molK). See the appendix in your text for other values.

$$2NH_3(g) + CO_2(g) \rightarrow NH_2CONH_2(aq) + H_2O(l)$$

S^o: **2 x 193** **214** **174** **70**

  - It is convenient to put the standard entropies (multiplied by their stoichiometric coefficients) below the formulas.

A Problem To Consider

- Calculate the change in entropy, ΔS^o, at 25 ^oC for the reaction in which urea is formed from NH_3 and CO_2. The standard entropy of NH_2CONH_2 is 174 J/(mol·K). See the appendix in your text for other values.

$$\mathbf{2NH_3(g) + CO_2(g) \rightarrow NH_2CONH_2(aq) + H_2O(l)}$$

  - We can now use the summation law to calculate the entropy change.

$$\Delta S^o = \sum n\Delta S^o(\text{products}) - \sum m\Delta S^o(\text{reactants})$$

A Problem To Consider

- Calculate the change in entropy, ΔS^o, at 25 ^oC for the reaction in which urea is formed from NH_3 and CO_2. The standard entropy of NH_2CONH_2 is 174 J/(mol·K). See the appendix in your text for other values.

$$\mathbf{2NH_3(g) + CO_2(g) \rightarrow NH_2CONH_2(aq) + H_2O(l)}$$

  - We can now use the summation law to calculate the entropy change.

$$\Delta S^o = [(174 + 70) - (2 \times 193 + 214)]\,J/K = -356\ J/K$$

Operational Skills

- **Calculating the entropy change for a phase transition**
- **Predicting the sign of the entropy change of a reaction**
- **Calculating ΔS^o for a reaction**

Time for a few review questions


TEACH
Peace
49