18.2: The First Law of Thermodynamics

The relationship between the energy change of a system and that of its surroundings is given by the first law of thermodynamicsThe energy of the universe is constant: $\Delta E_{universe} = \Delta E_{system} + \Delta E_{surroundings} = 0$., which states that the *energy of the universe is constant*. Using Equation 18.1.1, we can express this law mathematically as follows:

$$\Delta E_{univ} = \Delta E_{sys} + \Delta E_{surr} = 0 \tag{18.2.1}$$

$$\Delta E_{sys} = -\Delta E_{surr}$$

where the subscripts *univ*, *sys*, and *surr* refer to the universe, the system, and the surroundings, respectively. Thus the change in energy of a system is identical in magnitude but opposite in sign to the change in energy of its surroundings.

An important factor that determines the outcome of a chemical reaction is the tendency of all systems, chemical or otherwise, to move toward the lowest possible overall energy state. As a brick dropped from a rooftop falls, its potential energy is converted to kinetic energy; when it reaches ground level, it has achieved a state of lower potential energy. Anyone nearby will notice that energy is transferred to the surroundings as the noise of the impact reverberates and the dust rises when the brick hits the ground. Similarly, if a spark ignites a mixture of isooctane and oxygen in an internal combustion engine, carbon dioxide and water form spontaneously, while potential energy (in the form of the relative positions of atoms in the molecules) is released to the surroundings as heat and work. The internal energy content of the CO_2/H_2O product mixture is less than that of the isooctane/O_2 reactant mixture. The two cases differ, however, in the form in which the energy is released to the surroundings. In the case of the falling brick, the energy is transferred as work done on whatever happens to be in the path of the brick; in the case of burning isooctane, the energy can be released as solely heat (if the reaction is carried out in an open container) or as a mixture of heat and work (if the reaction is carried out in the cylinder of an internal combustion engine). Because heat and work are the only two ways in which energy can be transferred between a system and its surroundings, any change in the internal energy of the system is the sum of the heat transferred (*q*) and the work done (*w*):

$$\Delta E_{sys} = q + w \tag{18.2.2}$$

Although *q* and *w* are not state functions on their own, their sum (ΔE_{sys}) is independent of the path taken and is therefore a state function. A major task for the designers of any machine that converts energy to work is to maximize the amount of work obtained and minimize the amount of energy released to the environment as heat. An example is the combustion of coal to produce electricity. Although the maximum amount of energy available from the process is fixed by the energy content of the reactants and the products, the fraction of that energy that can be used to perform useful work is not fixed, as discussed in Section 18.5. Because we focus almost exclusively on the changes in the energy of a system, we will not use "sys" as a subscript unless we need to distinguish explicitly between a system and its surroundings.

Note the Pattern

The tendency of all systems, chemical or otherwise, is to move toward the state with the lowest possible energy.

Note the Pattern

Although *q* and *w* are not state functions, their sum (ΔE_{sys}) is independent of the path taken and therefore is a state function.

Example 18.2.1

A sample of an ideal gas in the cylinder of an engine is compressed from 400 mL to 50.0 mL during the compression stroke against a constant pressure of 8.00 atm. At the same time, 140 J of energy is transferred from the gas to the surroundings as heat. What is the total change in the internal energy (ΔE) of the gas in joules?

Given: initial volume, final volume, external pressure, and quantity of energy transferred as heat

Asked for: total change in internal energy

Strategy:

A Determine the sign of *q* to use in Equation 18.2.2.

B From Equation 18.1.5, calculate *w* from the values given. Substitute this value into Equation 18.2.2 to calculate ΔE.

Solution:

A From Equation 18.2.2, we know that $\Delta E = q + w$. We are given the magnitude of *q* (140 J) and need only determine its sign. Because energy is transferred from the system (the gas) to the surroundings, *q* is negative by convention.

B Because the gas is being compressed, we know that work is being done *on* the system, so *w* must be positive. From Equation 18.1.5,

$$w = -P_{ext}\Delta V = -\left(8.0 \ \cancel{atm}\right)\left(0.0500 \ \cancel{L} - 0.400 \ \cancel{L}\right)\left(\frac{101.3 \ J}{\cancel{L} \cdot \cancel{atm}}\right) = 284 \ J$$

Thus

$$\Delta E = q + w = -140 \ J + 284 \ J = 144 \ J$$

In this case, although work is done *on* the gas, increasing its internal energy, heat flows *from* the system *to* the surroundings, decreasing its internal energy by 144 J. The work done and the heat transferred can have opposite signs.

Exercise

A sample of an ideal gas is allowed to expand from an initial volume of 0.200 L to a final volume of 3.50 L against a constant external pressure of 0.995 atm. At the same time, 117 J of heat is transferred from the surroundings to the gas. What is the total change in the internal energy (ΔE) of the gas in joules?

Answer: −216 J

Note the Pattern

By convention, both heat flow and work have a negative sign when energy is transferred from a system to its surroundings and vice versa.

Enthalpy

To further understand the relationship between heat flow (*q*) and the resulting change in internal energy (ΔE), we can look at two sets of limiting conditions: reactions that occur at constant volume and reactions that occur at constant pressure. We will assume that *PV* work is the only kind of work possible for the system, so we can substitute its definition from Equation 18.1.5 into Equation 18.7 to obtain the following:

$$\Delta E = q - p\Delta V \tag{18.2.3}$$

where the subscripts have been deleted.

If the reaction occurs in a closed vessel, the volume of the system is fixed, and ΔV is zero. Under these conditions, the heat flow (often given the symbol q_v to indicate constant volume) must equal ΔE:

$$q_v = \Delta E \tag{18.2.4}$$
$$\text{\small constant volume}$$

No *PV* work can be done, and the change in the internal energy of the system is equal to the amount of heat transferred from the system to the surroundings or vice versa.

Many chemical reactions are not, however, carried out in sealed containers at constant volume but in open containers at a more or less constant pressure of about 1 atm. The heat flow under these conditions is given the symbol q_p to indicate constant pressure. Replacing *q* in Equation 18.2.3 by q_p and rearranging to solve for q_p,

$$q_p = \Delta E + P\Delta V \tag{18.2.5}$$
$$\text{\small constant pressure}$$

Thus, at constant pressure, the heat flow for any process is equal to the change in the internal energy of the system plus the *PV* work done, as we stated in Chapter 9.

Because conditions of constant pressure are so important in chemistry, a new state function called enthalpy (*H*)A state function that is the sum of the system's internal energy E and the product of its pressure P and volume V. H=E+PV is defined as $H = E + PV$. At constant pressure, the change in the enthalpy of a system is as follows:

$$\Delta H = \Delta E + \Delta (PV) = \Delta E + P\Delta (V) \tag{18.2.6}$$

Comparing the previous two equations shows that at constant pressure, the change in the enthalpy of a system is equal to the heat flow: $\Delta H = q_p$. This expression is consistent with our definition of enthalpy in Section Section 9.1, where we stated that enthalpy is the heat absorbed or produced during any process that occurs at constant pressure.

Note the Pattern

At constant pressure, the change in the enthalpy of a system is equal to the heat flow: $\Delta H = q_p$.

Example 18.2.2

The molar enthalpy of fusion for ice at 0.0°C and a pressure of 1.00 atm is 6.01 kJ, and the molar volumes of ice and water at 0°C are 0.0197 L and 0.0180 L, respectively. Calculate ΔH and ΔE for the melting of ice at 0.0°C. (For more information on enthalpy, see Section 9.2.)

Given: enthalpy of fusion for ice, pressure, and molar volumes of ice and water

Asked for: ΔH and ΔE for ice melting at 0.0°C

Strategy:

A Determine the sign of q and set this value equal to ΔH.

B Calculate $\Delta(PV)$ from the information given.

C Determine ΔE by substituting the calculated values into Equation 18.2.6.

Solution:

A Because 6.01 kJ of heat is absorbed from the surroundings when 1 mol of ice melts, $q = +6.01$ kJ. When the process is carried out at constant pressure, $q = q_p = \Delta H = 6.01$ kJ.

B To find ΔE using Equation 18.2.6, we need to calculate $\Delta(PV)$. The process is carried out at a constant pressure of 1.00 atm, so

$$\Delta PV = P\Delta V = P\left(V_f - V\right) = \left(1.00\ atm\right)\left(0.0180\ L - 0.0197\ lL\right)$$

$$= \left(-1.7 \times 10-3\ L \cdot \cancel{atm}\right)\left(101.3\ J/\ L \cdot \cancel{atm}\right)$$

C Substituting the calculated values of ΔH and $P\Delta V$ into Equation 18.2.6,

$$\Delta E = \Delta H - P\Delta V = -6010\ J - \left(-0.0017\ J\right) = 6010\ J = 6.01\ kJ$$

Exercise

At 298 K and 1 atm, the conversion of graphite to diamond requires the input of 1.850 kJ of heat per mole of carbon. The molar volumes of graphite and diamond are 0.00534 L and 0.00342 L, respectively. Calculate ΔH and ΔE for the conversion of C (graphite) to C (diamond) under these conditions.

Answer: $\Delta H = 1.85$ kJ/mol; $\Delta E = 1.85$ kJ/mol

The Relationship between ΔH and ΔE

If ΔH for a reaction is known, we can use the change in the enthalpy of the system (Equation 18.2.6) to calculate its change in internal energy. When a reaction involves only solids, liquids, liquid solutions, or any combination of these, the volume does not change appreciably ($\Delta V = 0$). Under these conditions, we can simplify Equation 18.2.6 to $\Delta H = \Delta E$. If gases are involved, however, ΔH and ΔE can differ significantly. We can calculate ΔE from the measured value of ΔH by using the right side of Equation 18.11 together with the ideal gas law, $PV = nRT$. Recognizing that $\Delta(PV) = \Delta(nRT)$, we can rewrite Equation 18.2.6 as follows:

$$\Delta H = \Delta E + \Delta\left(PV\right) = \Delta E + \Delta\left(nRT\right) \tag{18.2.7}$$

At constant temperature, $\Delta(nRT) = RT\Delta n$, where Δn is the difference between the final and initial numbers of moles of gas. Thus

$$\Delta E = \Delta H - RT\Delta n \tag{18.2.8}$$

For reactions that result in a net production of gas, $\Delta n > 0$, so $\Delta E < \Delta H$. Conversely, endothermic reactions ($\Delta H > 0$) that result in a net consumption of gas have $\Delta n < 0$ and $\Delta E > \Delta H$. The relationship between ΔH and ΔE for systems involving gases is illustrated in Example 4.

Note the Pattern

For reactions that result in a net production of gas, $\Delta E < \Delta H$. For endothermic reactions that result in a net consumption of gas, $\Delta E > \Delta H$.

Example 18.2.3

The combustion of graphite to produce carbon dioxide is described by the equation C (graphite, s) + O_2(g) → CO_2(g). At 298 K and 1.0 atm, ΔH = −393.5 kJ/mol of graphite for this reaction, and the molar volume of graphite is 0.0053 L. What is ΔE for the reaction?

Given: balanced chemical equation, temperature, pressure, ΔH, and molar volume of reactant

Asked for: ΔE

Strategy:

A Use the balanced chemical equation to calculate the change in the number of moles of gas during the reaction.

B Substitute this value and the data given into Equation 18.2.8 to obtain ΔE.

Solution:

A In this reaction, 1 mol of gas (CO_2) is produced, and 1 mol of gas (O_2) is consumed. Thus Δn = 1 − 1 = 0.

B Substituting this calculated value and the given values into Equation 18.2.8,

$$\Delta E = \Delta H - RT\Delta n = (-393.5 \ kJ/mol) - [8.314 \ J/mol \cdot K]\,(298 \ K)\,(0)$$

$$= (-393.5 \ kJ/mol) - (0 \ J/mol) = -393.5 \ kJ$$

To understand why only the change in the volume of the gases needs to be considered, notice that the molar volume of graphite is only 0.0053 L. A change in the number of moles of gas corresponds to a volume change of 22.4 L/mol of gas at standard temperature and pressure (STP), so the volume of gas consumed or produced in this case is (1)(22.4 L) = 22.4 L, which is much, much greater than the volume of 1 mol of a solid such as graphite.

Exercise

Calculate ΔE for the conversion of oxygen gas to ozone at 298 K: $3O_2$(g) → $2O_3$(g). The value of ΔH for the reaction is 285.4 kJ.

Answer: 288 kJ

As the exercise in Example 4 illustrates, the magnitudes of ΔH and ΔE for reactions that involve gases are generally rather similar, even when there is a net production or consumption of gases.

Summary

The **first law of thermodynamics** states that the energy of the universe is constant. The change in the internal energy of a system is the sum of the heat transferred and the work done. At constant pressure, heat flow (q) and internal energy (E) are related to the system's **enthalpy (H)**. The heat flow is equal to the change in the internal energy of the system plus the PV work done. When the volume of a system is constant, changes in its internal energy can be calculated by substituting the ideal gas law into the equation for ΔE.

Key Takeaway

- Enthalpy is a state function, and the change in enthalpy of a system is equal to the sum of the change in the internal energy of the system and the PV work done.

Key Equations

Internal energy change

Equation 18.2.2: $\Delta E_{sys} = q + w$

Enthalpy change

Equation 18.2.6: $\Delta H = \Delta E + \Delta(PV)$

Relationship between Δ H and Δ E for an ideal gas

Equation 18.2.8: $\Delta E = \Delta H - RT\Delta n$
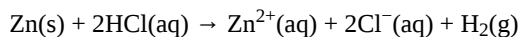
Conceptual Problems

1. Describe how a swinging pendulum that slows with time illustrates the first law of thermodynamics.

2. When air is pumped into a bicycle tire, the air is compressed. Assuming that the volume is constant, express the change in internal energy in terms of q and w.

3. What is the relationship between enthalpy and internal energy for a reaction that occurs at constant pressure?

4. An intrepid scientist placed an unknown salt in a small amount of water. All the salt dissolved in the water, and the temperature of the solution dropped several degrees.

    1. What is the sign of the enthalpy change for this reaction?
    2. Assuming the heat capacity of the solution is the same as that of pure water, how would the scientist calculate the molar enthalpy change?
    3. Propose an explanation for the decrease in temperature.

5. For years, chemists and physicists focused on enthalpy changes as a way to measure the spontaneity of a reaction. What arguments would you use to convince them not to use this method?

6. What is the relationship between enthalpy and internal energy for a reaction that occurs at constant volume?

7. The *enthalpy of combustion* (ΔH_{comb}) is defined thermodynamically as the enthalpy change for complete oxidation. The complete oxidation of hydrocarbons is represented by the following general equation: hydrocarbon + $O_2(g)$ → $CO_2(g)$ + $H_2O(g)$. Enthalpies of combustion from reactions like this one can be measured experimentally with a high degree of precision. It has been found that the less stable the reactant, the more heat is evolved, so the more negative the value of ΔH_{comb}. In each pair of hydrocarbons, which member do you expect to have the greater (more negative) heat of combustion? Justify your answers.

    1. cyclopropane or cyclopentane
    2. butane or 2-methylpropane
    3. hexane or cyclohexane

8. Using a structural argument, explain why the *trans* isomer of 2-butene is more stable than the *cis* isomer. The enthalpies of formation of *cis*- and *trans*-2-butene are −7.1 kJ/mol and −11.4 kJ/mol, respectively.

9. Using structural arguments, explain why cyclopropane has a positive $\Delta H_f°$ (12.7 kJ/mol), whereas cyclopentane has a negative $\Delta H_f°$ (−18.4 kJ/mol). (Hint: consider bond angles.)

Answers

1.
2.
3. At constant pressure, $\Delta H = \Delta E + P\Delta V$.

4.
5.
6.
7.
8.
9. With bond angles of 60°, cyclopropane is highly strained, causing it to be less stable than cyclopentane, which has nearly ideal tetrahedral geometry at each carbon atom.
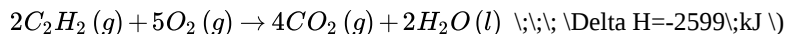
Numerical Problems

1. A block of CO_2 weighing 15 g evaporates in a 5.0 L container at 25°C. How much work has been done if the gas is allowed to expand against an external pressure of 0.98 atm under isothermal conditions? The enthalpy of sublimation of CO_2 is 25.1 kJ/mol. What is the change in internal energy (kJ/mol) for the sublimation of CO_2 under these conditions?

2. Zinc and HCl react according to the following equation:

$Zn(s) + 2HCl(aq) \rightarrow Zn^{2+}(aq) + 2Cl^-(aq) + H_2(g)$

When 3.00 g of zinc metal is added to a dilute HCl solution at 1.00 atm and 25°C, and this reaction is allowed to go to completion at constant pressure, 6.99 kJ of heat must be removed to return the final solution to its original temperature. What are the values of q and w, and what is the change in internal energy?

3. Acetylene torches, used industrially to cut and weld metals, reach flame temperatures as high as 3000°C. The combustion reaction is as follows:

$$2C_2H_2(g) + 5O_2(g) \rightarrow 4CO_2(g) + 2H_2O(l) \;\;\; \Delta H = -2599 \; kJ$$

Calculate the amount of work done against a pressure of 1.0 atm when 4.0 mol of acetylene are allowed to react with 10 mol of O_2 at 1.0 atm at 20°C. What is the change in internal energy for the reaction?

4. When iron dissolves in 1.00 M aqueous HCl, the products are FeCl$_2$(aq) and hydrogen gas. Calculate the work done if 30 g of Fe react with excess hydrochloric acid in a closed vessel at 20°C. How much work is done if the reaction takes place in an open vessel with an external pressure of 1.0 atm?

Answer

1. −350 J; 8.2 kJ

2.

3.

4.

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