Name: **Date:** KEY

§ 06.03.b1 Energy: 1st Law of Thermodynamics – Useful Applications

Most Important Ideas:

1. 1st law of thermodynamics = law of conservation of mass-energy:
   $\Delta E_{system} + \Delta E_{surroundings} = 0$ (ΔE = change in energy)
2. $\Delta E = q + w$ (q = heat; w = work)
3. $w = -P\Delta V$ (P = pressure, atm; ΔV = change in volume, L)

Objective

The objective of this activity is to be able to convert from one form of energy (e.g., work) to another form of energy (e.g., moving a piston).

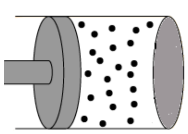
Background

Thermodynamics is the study of the conversion between heat and other types of energy. The first law of thermodynamics states that energy can be converted from one form to another, but can't be created or destroyed.[1] The internal energy of a system (ΔE) has potential and kinetic energies. For example, before a candle is lit, it has only potential energy in the form of chemical energy. Once lit, it has kinetic energy (e.g., heat and light) as well whatever chemical energy (candle) is left. The loss of stored chemical energy equals the energy released. And the total energy in the universe remains unchanged. The system is the substances we are studying (e.g., solution + beaker). The surroundings are rest of the universe.

It is impossible to measure exactly the internal energy of a system. Therefore, we measure the changes in energy by experiment. The change in energy (ΔE) is the sum of released energy in the form of heat and work.

$$\boxed{\Delta E = q + w}$$

By definition, work = force x distance. In chemistry, work typically involves the increase in pressure or the change in volume of a piston.



$w = f * d$

force = P

distance = ΔV

Therefore:

$$\boxed{w = -P\Delta V}$$

N.B.

1. *It will help you if you can first draw a picture.*
2. *Energy (e.g., heat and work) is expressed in joules (J):* $\boxed{\textit{1 L*atm = 101.3 joule}}$
3. *The sign of work is negative when work is done by the system (e.g., piston expands, w = –6 J)*
4. *The sign of heat is negative when heat is released (i.e., exothermic) (e.g., q = – 10 J)*

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[1] Energy and mass are related by E = mc2. However, because we are not performing any nuclear reactions, we use the law as stated above.

***Model - 1*[2]**

Problem

A certain gas expands in volume from 2.0 L to 6.0 L at a constant temperature. Calculate the work done by the gas if it expands (a) against a vacuum and (b) against a constant pressure of 1.2 atm.

Strategy

Equation: $w = -P\Delta V$

a. Because there is no pressure (P = 0 atm in a vacuum), w = 0

b. $w = -P\Delta V$ $\quad w = -(1.2\ atm)(6.0\ L - 2.0\ L)$

$$w = 4.8\ L{*}atm$$

$$w = \frac{-4.8\ L * atm}{} x \frac{101.3\ J}{1\ L * atm}$$

$$w = -4.9\ x\ 10^2\ J$$

Model - 2

Problem

The work done when a gas is compressed in a cylinder is 387 J. During this process, there is a heat transfer of 152 J from the gas to the surroundings. Calculate he energy change for this process.

Strategy

We are dealing with energy (ΔE) and both heat (q) and work (w). Because work is done on the system, ΔE is positive.

$\Delta E = q + w$ $\quad \Delta E = (387\ J)\ (152\ J)$

$$\Delta E = 235\ J$$

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[2] Example 6.1, Chang & Overby, 6th edition.

Problems

1. A gas expands from 264 mL to 971 mL at a constant temperature. Calculate the work (J) done by the gas if it expands (a) against a vacuum and (b) against a constant pressure of 4.00 atm.

Recall that the work in gas expansion is equal to the product of the external, opposing pressure and the change in volume.

(a) $w = -P\Delta V$

$\mathbf{w} = -(0)(0.971 - 0.264)\text{L} = \mathbf{0}$

(b) $w = -P\Delta V$

$w = -(4.00 \text{ atm})(0.971 - 0.264)\text{L} = -2.83 \text{ L·atm}$

To convert the answer to joules, we write

$$w = -2.83\ L.atm\ x\ \frac{101.3\ J}{1\ L.atm} = -2.86\ x\ 10^2\ J$$

2. A sample of nitrogen gas expands in volume from 1.6 L to 5.4 L at a constant temperature. Calculate the work (J) if the gas expands (a) against a vacuum, (b) against a constant pressure of 0.80 atm, and (c) against a constant pressure of 3.7 atm.

Recall that the work in gas expansion is equal to the product of the external, opposing pressure and the change in volume.

(a) $w = -P\Delta V$

$\mathbf{w} = -(0)(5.4 - 1.6)\text{L} = \mathbf{0}$

(b) $w = -P\Delta V$

$w = -(0.80 \text{ atm})(5.4 - 1.6)\text{L} = -3.0 \text{ L·atm}$

To convert the answer to joules, we write

$$\mathbf{w} = -3.0\ \cancel{\text{L}}\cdot\cancel{\text{atm}} \times \frac{101.3\ \text{J}}{1\ \cancel{\text{L}}\cdot\cancel{\text{atm}}} = \mathbf{-3.0 \times 10^2\ J}$$

(c) $w = -P\Delta V$

$w = -(3.7 \text{ atm})(5.4 - 1.6)\text{L} = -14 \text{ L·atm}$

To convert the answer to joules, we write

$$\mathbf{w} = -14\ \cancel{\text{L}}\cdot\cancel{\text{atm}} \times \frac{101.3\ \text{J}}{1\ \cancel{\text{L}}\cdot\cancel{\text{atm}}} = \mathbf{-1.4 \times 10^3\ J}$$

3. A gas expands in volume from 26.7 mL to 89.3 mL at constant temperature. Calculate the work done (J) if the gas expands against a vacuum, (b) against a constant pressure of 1.5 atm, and (c) against a constant pressure of 2.8 atm.

   (a) Because the external pressure is zero, no work is done in the expansion.

$$w = -P\Delta V = -(0)(89.3 - 26.7)\text{mL}$$

$$\boldsymbol{w = 0}$$

   (b) The external, opposing pressure is 1.5 atm, so

$$w = -P\Delta V = -(1.5\ \text{atm})(89.3 - 26.7)\text{mL}$$

$$w = -94\ \cancel{\text{mL}}\cdot\text{atm} \times \frac{0.001\ \text{L}}{1\ \cancel{\text{mL}}} = -0.094\ \text{L}\cdot\text{atm}$$

   To convert the answer to joules, we write:

$$\boldsymbol{w} = -0.094\ \cancel{\text{L}}\cdot\cancel{\text{atm}} \times \frac{101.3\ \text{J}}{1\ \cancel{\text{L}}\cdot\cancel{\text{atm}}} = \mathbf{-9.5\ J}$$

   (c) The external, opposing pressure is 2.8 atm, so

$$w = -P\Delta V = -(2.8\ \text{atm})(89.3 - 26.7)\text{mL}$$

$$w = (-1.8 \times 10^2\ \cancel{\text{mL}}\cdot\text{atm}) \times \frac{0.001\ \text{L}}{1\ \cancel{\text{mL}}} = -0.18\ \text{L}\cdot\text{atm}$$

   To convert the answer to joules, we write:

$$\boldsymbol{w} = -0.18\ \cancel{\text{L}}\cdot\cancel{\text{atm}} \times \frac{101.3\ \text{J}}{1\ \cancel{\text{L}}\cdot\cancel{\text{atm}}} = \mathbf{-18\ J}$$

4. A gas expands and does P-V work on the surroundings equal to 325 J. At the same time, it absorbs 127 J of heat from the surroundings. Calculate the change in energy of the gas.

$$\boldsymbol{\Delta U} = q + w = 127\ \text{J} - 325\ \text{J} = \mathbf{-198\ J}$$

5. The work done to compress a gas is 74 J. As a result, 26 J of heat is given off to the surroundings. Calculate the change in energy (J) of the gas.

Strategy: Compression is work done on the gas, so what is the sign for w? Heat is released by the gas to the surroundings. Is this an endothermic or exothermic process? What is the sign for q?

Solution: To calculate the energy change of the gas (ΔU), we need Equation (6.1) of the text. Work of compression is positive and because heat is given off by the gas, q is negative. Therefore, we have:

$$\boldsymbol{\Delta U} = q + w = -26\ \text{J} + 74\ \text{J} = \mathbf{48\ J}$$

As a result, the energy of the gas increases by 48 J.

6. Calculate the work done when 50.0 g of tin dissolves in an excess of acid at 1.00 atm and 25°C.

$$Sn(s) + 2H^{+}(aq) \rightarrow Sn^{2+}(aq) + H_2(g)$$

We first find the number of moles of hydrogen gas formed in the reaction:

$$50.0\ \cancel{g}\ Sn \times \frac{1\ \cancel{mol}\ Sn}{118.7\ \cancel{g}\ Sn} \times \frac{1\ mol\ H_2}{1\ \cancel{mol}\ Sn} = 0.421\ mol\ H_2$$

The next step is to find the volume occupied by the hydrogen gas under the given conditions. This is the change in volume.

$$V = \frac{nRT}{P} = \frac{(0.421\ \cancel{mol})(0.0821\ L \cdot \cancel{atm} / \cancel{K} \cdot \cancel{mol})(298\ \cancel{K})}{1.00\ \cancel{atm}} = 10.3\ L\ H_2$$

The pressure-volume work done is then:

$$\boldsymbol{w} = -P\Delta V = -(1.00\ atm)(10.3\ L) = -10.3\ \cancel{L} \cdot \cancel{atm} \times \frac{101.3\ J}{1\ \cancel{L} \cdot \cancel{atm}} = \mathbf{-1.04 \times 10^{3}\ J}$$

7. Calculate the work (J) when 1.0 mole of water vaporizes at 1.0 atm and 100oC. Assume the volume of the liquid is negligible compared to that of steam at 100°C, and has ideal gas behavior.

Strategy: The work done in gas expansion is equal to the product of the external, opposing pressure and the change in volume.

$$w = -P\Delta V$$

We assume that the volume of liquid water is zero compared to that of steam. How do we calculate the volume of the steam? What is the conversion factor between L·atm and J?

Solution: First, we need to calculate the volume that the water vapor will occupy (V_f).

Using the ideal gas equation:

$$V_{H_2O} = \frac{n_{H_2O}RT}{P} = \frac{(1\ \cancel{\text{mol}})\left(0.0821\frac{\text{L}\cdot\cancel{\text{atm}}}{\cancel{\text{mol}}\cdot\cancel{\text{K}}}\right)(373\ \cancel{\text{K}})}{(1.0\ \cancel{\text{atm}})} = 31\text{ L}$$

It is given that the volume occupied by liquid water is negligible. Therefore,

$$\Delta V = V_f - V_i = 31\text{ L} - 0\text{ L} = 31\text{ L}$$

Now, we substitute P and ΔV into Equation (6.3) of the text to solve for w.

$$w = -P\Delta V = -(1.0\text{ atm})(31\text{ L}) = -31\text{ L·atm}$$

The problems asks for the work done in units of joules. The following conversion factor can be obtained from Appendix 1 of the text.

$$1\text{ L·atm} = 101.3\text{ J}$$

Thus, we can write:

$$\boldsymbol{w} = -31\ \cancel{\text{L}}\cdot\cancel{\text{atm}} \times \frac{101.3\text{ J}}{1\ \cancel{\text{L}}\cdot\cancel{\text{atm}}} = \mathbf{-3.1 \times 10^3\ J}$$

Check: Because this is gas expansion (work is done by the system on the surroundings), the work done has a negative sign.

Extension

8. Calculate ΔE when a gas absorbs 18 J of heat and has 13 J of work done on it.

   heat absorbed = +18 J (heat absorbed has '+' sign)
   word done on it = +13 J (energy absorbed has '+' sign)

   ΔE = q + w

   ΔE = (+18 J) + (+13 J)

   ΔE = 31 J

9. Consider the following reaction for three substances (X, Y, and Z) in a moveable piston

$$X(g) + Y(g) \rightarrow Z(l)$$

   As the reaction occurs, the system loses 1185 J of heat. The piston moves down and surroundings do 623 J of work on the system. What is ΔE?

   heat released by system: = –1185 J
   work done on system: = + 623 J

   ΔE = q + w

   ΔE = (–1185 J) + (+623 J)

   ΔE = –562 J

10. A chemical reaction occurs in a cylinder, with a moveable piston, at a constant pressure of 1.2 atm and temperature of 25°C. The change in energy is –436J. What is the change in volume of the cylinder?

   ΔE = q + w   w = –PΔV   ⇒ ΔE = q – PΔV   ⇒ $\Delta V = \frac{q - \Delta E}{P}$

   P = 1.2 atm

$$\Delta E = \frac{-436\,J}{} x \frac{1\,L - atm}{101.3\,J} = -4.30\,L - atm$$

   q = 0

$$\Delta V = \frac{-4.30\,L * atm}{1.2\,atm} = -3.59\,L$$