Skills to Develop

Be able to apply the following key equations for problem solving:

\[ dE = q + w \]
\[ w = d(P \cdot V) \]
\[ w = -P \cdot dV \] (constant P, negative sign to take care of sign in dV)
\[ H = E + P \cdot V \]
\[ dH = dE + P \cdot dV \]
\[ q = dH_{\text{p}} \] (for constant P)
\[
\begin{align}
q &= \text{specific heat} \times \text{mass} \times dT \\
&= s \cdot m \cdot dT
\end{align}
\]
\[
\begin{align}
q &= C \times dT \\
&(C, \text{ heat capacity})
\end{align}
\]
\[ q = dE \] (for constant V)
\[ P \cdot dV = dn \cdot R \cdot T \]
\[ dH = dE + dn \cdot R \cdot T \]

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Thermochemistry - A Review

Thermochemistry is the study of energy changes accompanying chemical and physical reactions. The purpose of this page is to give a brief summary of concepts on thermochemistry to be tested in the quiz.

This page is very similar to weekly skill review. Using either page will be fine.

Energy

Energy is the potential to do work, such as accelerating an object (kinetic energy), lifting things up (potential energy), producing electric power (electric energy), raising the temperature of a system (heat) and producing sound (waves of energy). In physics, work is formally defined as force times the distance in the direction of the force, and such a definition defines the very basic idea of energy.

Energy is the driving force of changes. All changes are caused by energy, and the cause or energy can be in many forms: light, heat, work, electrical, mechanical (energy stored in a spring), chemical, etc. The changes are phenomena caused by energy, but more importantly, forms of energy inter-convert into one another during the changes.

Unlike some of these changes, forms of energy convert into one another always at a fixed rate. Exactly 4.184 J of
mechanical work converts into 1.00 cal measured as heat, and vice versa.

**Conservation of Energy**

Energy can neither be destroyed, nor created; it converts from one form (for example heat) to another form (say mechanical work) at a fixed rate. This is the fundamental principle of conservation of energy.

To indicate changes, we use \(d\) to represent the delta (\(D\)) commonly used in textbooks, because using the delta will cause the loading of this page into your computer to be very slow.

The internal energy \(E\) accounts for energy and work transferred to a system. This concept is another form of the principle of conservation of energy. The change in internal energy \(dE\) of a closed system increases by the amount of energy input to the system. Such input can be in the form of heat \(q\) or (mechanical or any other form) of work \(w\). Usually, it is formulated as

\[
(dE = q + w).
\]

Heat transferred out and work done by the system are assigned negative signs by convention. This relationship is usually referred to as the first law of thermodynamics.

When energy is transferred from system A to system B, what happens to the energy? Does energy disappear? The internal energy as defined above shows that energy does not disappear, because the internal energy loss of system A equals the internal energy gain of system B. The change in internal energy, \(dE\), is negative for system A, but positive for system B. Energy is neither destroyed, nor created.

**Heats of Reactions**

The enthalpy of reaction, \(dH\), is the energy [heat \((q)\) and work \((d(P V))\)] released in a reaction. The thermochemical equation is usually written in the form:

\[
2\text{H}_2(g, \text{1 atm}) + O_2(g) \rightarrow 2\text{H}_2O(l), \quad \mathit{dH} = -571.7\text{ kJ}
\]

This equation means that when 2 moles of \(\text{H}_2(g)\) gas react with 1 mole of \(\text{O}_2(g)\) gas, 571.7 kJ of energy is released (lost to the surrounding). Thus, if 1 mole of \(\text{H}_2(g)\) and one half mole of \(\text{O}_2(g)\) react, half of 571.7 kJ or 285.9 kJ of energy is released.

\[
\text{H}_2(g, \text{1 atm}) + 0.5\text{O}_2 \rightarrow \text{H}_2O(l), \quad \mathit{dH} = -285.9\text{ kJ}
\]

On the other hand, if double amounts of reactants (i.e. 4 moles of \(\text{H}_2(g)\) and 2 moles of \(\text{O}_2(g)\)) are used, twice the amount of energy \((2^\times(-571.7) = -1043.4\text{ kJ})\) is released.

If \(dH\) is positive, at least that much energy must be supplied to carry out the endothermic reaction.

**The Standard Enthalpy of Reaction**

For convenience in application, 1 atm for gas and 1.0 M for solutions were considered the "standard conditions", and
data collected at standard conditions were called standard data such as standard enthalpy of reaction and standard enthalpy of formation. These values are condensed and summarized in handbooks for scientists and engineers in their applications.

Because temperature, pressure, and concentration of reactants and products affect the amount of measured energy, the scientific community has agreed upon a temperature of 273 K and 1 atm as the standard temperature and pressure (STP). However, standard enthalpies are often given for data collected at 298 K.

The most stable state at the standard condition is the standard state. The enthalpy of an element at its standard state is assigned 0 for reference.

For example, at 1 atm, graphite is the most stable state of carbon. The standard enthalpy of combustion of carbon is the energy released (-394 kJ) when 1 mole of graphite reacts with oxygen in the reaction

\[ \text{C}_{\text{(graphite)}} + \text{O}_2 \rightarrow \text{CO}_2, \quad dH^o = -394 \text{ kJ} \]

Since the measurement is done at the standard condition, a superscript o is usually placed on the right side of \( H \) in most literature. Incidentally, the above equation is for the formation of \( \text{CO}_2 \), and the enthalpy of reaction happens to be the enthalpy of formation of \( \text{CO}_2 \), designated as \( dH^o_f = -394 \text{ kJ} \), as reviewed in the next paragraph.

As another example, when 1.0 mole \( \text{Zn} \) reacts with sufficient amount of \( \text{HCl} \) solution (1.0 M), 150 kJ is released. Thus, we write standard energy of reaction for \( \text{Zn} \) as,

\[ \text{Zn} + 2 \text{HCl}_{\text{(aq)}} \rightarrow \text{H}_2 + \text{ZnCl}_{2\text{(aq)}}, \quad dH^o = -150 \text{ kJ} \]

The Standard Enthalpy of Formation

Combination of elements at their standard states resulting in one compound is called a formation reaction. When enthalpy of formation is measured at the standard condition, it is called the standard enthalpy of formation. The standard enthalpy of combustion of carbon mentioned earlier

\[ \text{C}_{\text{(graphite)}} + \text{O}_2 \rightarrow \text{CO}_2, \quad dH^o_f = -394 \text{ kJ} \]

is the formation of \( \text{CO}_2 \) from elements at their standard states. Thus, \( dH^o_f \) of -394 kJ is also the standard enthalpy of formation of \( \text{CO}_2 \).

Similarly, a few more examples are given below. The enthalpies can be both positive and negative values.

\[ \text{O}_2 = \text{O}, \quad dH^o_f = 249.17 \text{ kJ} \]
\[ \text{H}_2 = \text{H}, \quad dH^o_f = 217.96 \text{ kJ} \]
\[ \text{H}_2 + \text{O}_2 = \text{H}_2\text{O}_{\text{(aq)}}, \quad dH^o_f = -191.76 \text{ kJ} \]
\[ \text{H}_2 + \text{Cl}_2 = \text{HCl}_{\text{(g)}}, \quad dH^o_f = -92.31 \text{ kJ} \]
\[ \text{H}_2 + \text{Br}_2 = \text{HBr}_{\text{(g)}}, \quad dH^o_f = -36.40 \text{ kJ} \]
Hess's Law

Hess's law is another interpretation of the principle of conservation of energy. Since the changes in energy are independent of path, they depend on the initial and final state of the system. Thus, if it takes several steps to reach the final state from the initial state, the changes in energy are additive. The law states:

*The total enthalpy change in a reaction is the same whether the reaction occurs in one or several steps.*

However, one should recognize that the enthalpy change is related to the amounts of reactants and products in the equation.

A simple application of Hess's law is to give the standard enthalpy of decomposition of \(\ce{CO2\rightarrow C_{(graphite)} + O_{2\(g\)}}\) from its standard enthalpy of formation,

\[
\ce{\text{CO}_{2\(g\)} \rightarrow \text{C}_{(graphite)} + \text{O}_{2\(g\)}, \ \Delta H^\circ = 394 \text{ kJ}}
\]

Note that we change the sign of \(\Delta H^\circ\) if the reaction is reversed.

Measurements of Energy Changes

Various experimental techniques have been designed to measure energy changes in a chemical reaction. It is necessary to know the heat capacity of a system. Precise measurements require carefully designed calorimeters.

Enthalpy of reaction (\(\Delta H\)) is measured when the reaction is carried out at constant pressure. When a bomb calorimeter is used, the volume does not change. The amount of energy measured is the internal energy \(\Delta E\). To convert \(\Delta E\) into \(\Delta H\), we use the defined relationship,

\[
\Delta H = \Delta E + \text{d}(P V).
\]

The changes in pressure and volume (\(P V\)) work can be evaluated by the application of ideal gas law,

\[
\text{d}(P V) = dn R T,
\]

where \(dn\) is the total number of moles of gas of product \(Sn\) (products) minus the total number of moles of gas of reactants, \(Sn\) (reactants).

\[
\Delta n = Sn(\text{products}) - Sn(\text{reactants})
\]

Example 1

Will the reaction

\[
\ce{P_4O_{10\(s\)} + 6 H_2O_{\(l\)} \rightarrow 4 H_2PO_{4\(aq\)}}
\]

be exothermic or endothermic?
**Solution**

The enthalpy of a reaction can be evaluated from the standard enthalpies of formation of all products and reactants.

\[
\Delta H^o = \Delta H^o_f(\text{all: products}) - \Delta H^o_f(\text{all: reactants})
\]

Thus, it is desirable to find the \( \Delta H^o_f \) of all products and reactants: \( \ce{P4O10} \), -3110 kJ/mol; \( \ce{H2} \), -286 kJ/mol; \( \ce{H3PO4} \), -1288 kJ/mol.

\[
\begin{align*}
\Delta H^o &= -4\times1288 - (-3110 -286\times6) \\
&= -326 \text{ kJ/mol}
\end{align*}
\]

**Discussion**

The entropy (\( \Delta S \)) is another important piece of thermodynamic data, which is often listed together with \( \Delta H^o \). The entropies are: \( \ce{P4O10} \), 229 J/(K mol); \( \ce{H2} \), 70 J/(K mol); \( \ce{H3PO4} \), 158 J/(K mol); and the entropy of the reaction is thus:

\[
\begin{align*}
\Delta S &= 4\times158 - (6\times70 + 229) \text{ kJ/mol} \\
&= -17 \text{ J/(K mol)}
\end{align*}
\]

and the Gibb's free energy \( \Delta G = \Delta H - T\Delta S \),

\[
\begin{align*}
\Delta G &= [-326 - 298 \times (-0.017)] \text{ kJ/mol} \\
&= -321 \text{ kJ/mol}
\end{align*}
\]

A negative value for \( \Delta G \) indicates that the reaction will be spontaneous.

Don't worry. General chemistry students are not expected to know entropy and Gibb's free energy yet.

A summary of thermochemistry has been given. Thermochemistry deals with the energy aspect of chemical reactions. A more complete study of energy is Thermodynamics. This link is divided into 7 units: Energy, Enthalpy, Hess's Law, Enthalpy of Formation, Entropy, Gibbs Free Energy and Conclusion. You may find its simple approach interesting. Some of the aspect has been included in the discussion of the above example.

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**Confidence Building Questions**

1. **A person weighing 65 kg climbed 11 m up a rope; how much work (in kJ) was involved? (g = 9.8 ms\(^{-2}\))**

   Hint: 7.0 kJ
Skill:
Calculate mechanical work or energy involved.
In reality, more energy is required due to low efficiency of energy utilization.

2. Assume the ideal gas law. What is the volume occupied by 1.00 mole (18.0 g) of water vapor at its boiling point, 373 K at a pressure of 1 atm? ($R = 0.08205 \text{L atm/(mol K)}$)

Hint: 30.6 L

Discussion
Molar volume is 30.6 L at 373 K, but 22.4 L at STP. Water is a liquid at STP, and its vapor pressure is very low.

3. When water boils, the vapor expands against a constant atmospheric pressure of 1 atm. Calculate the work (J) done by one mole of water vapor if its volume is 30.6 L.

(1 atm = 101.3 kPa, $R = 8.314 \text{J/(mol K)}$, $1 \text{L} = 0.001 \text{m}^3$)

Hint: -3100 J

Skill:
Calculate pressure-volume work.

4. The heat of vaporization for one mole of water is 40.7 kJ (i.e., 40.7 kJ absorbed by 18 g of $\ce{H2O}$). If 3.1 kJ of work is done by the system, what is the increase in internal energy $dE$?

Hint: 37.6 kJ

Skill:
Evaluate internal energy.
When water evaporates, its vapor occupies 30.6 L at 373K, and work is done by pushing its way in the atmosphere of 1 atm. $0.0306 \times 101.3 = 3.1 \text{kJ}$

5. Let us consider the condensation of water vapor, or gas $\ce{H2O}$. A $\ce{H2O}$ gas loses 40.7 kJ of heat when it condenses, and the environment performs 3.1 kJ of work when the volume contracts. Calculate the gain (or loss) (negative change) in internal energy (kJ).

Hint: -37.6 kJ

Discussion
This problem states the reversed process of the previous problem.

6. A battery does 63 J of electrical work and loses 3.0 J of heat. Which of the following (all in unit J) ARE correct:
   a. $dE = 66$
   b. $dE = -60$
   c. $dE = 63$
   d. $dE = -66$
e. $w = 63$

f. $w = -63$

g. $w = 60$

h. $w = -66$

i. $q = 3$

j. $q = -3$

k. $q = 60$

l. $q = -60$

Hint: d f & j are all true.

Skill:
Various skills are involved.

7. It is known that 1.0 cal is equivalent to 4.184 J, and 40.7 kJ is required to evaporate 1.0 mol of $\text{H}_2\text{O}$ (molar mass, 18.0). Calculate the heat (in cal) required to evaporate 1.0 g $\text{H}_2\text{O}$.

Hint: 540 cal

A reminder of unit conversion:

$$40700 \dfrac{J}{mol} \times \dfrac{1}{4.184 \dfrac{J}{cal}} \times \dfrac{1}{18 \text{ g}} = 540 \text{ cal}$$

8. What is the sign of the enthalpy change for the following reaction?

$$2 \text{ CO} + \text{ O}_2 \rightarrow 2\text{CO}_2$$

Positive or negative?

Hint: negative

Skill:
Explain exothermic and endothermic reactions in terms of enthalpy of reaction.

9. Given the following standard enthalpies (kJ) of formation at 25 °C,

$$\text{NH}_3, -46.1; \text{CO}_2, -393.5; \text{C}_2\text{H}_4, 52.3; \text{NO}_2, 33.2$$

which molecule will require the most energy to form?

Hint: $\text{C}_2\text{H}_4$

Skill:
Explain the meaning of enthalpy.

10. Given the following enthalpies (kJ) of formation,
calculate the enthalpy change for the reaction:
\[
\text{2 H}_2\text{S} + \text{SO}_2 \rightarrow 3 \text{S} + 2 \text{H}_2\text{O} \hspace{15px} \text{dH} = \text{?}
\]
All reactants and products are in their standard states.
Hint: -233.6 kJ

Skill:
Evaluate the standard enthalpy of reaction from standard enthalpies of formation of reactants and products.

Further hint
Writing all the equations out presents the evaluation in a logical way.

\[
\begin{align*}
\text{2 H}_2 + \text{O} \rightarrow 2 \text{H}_2\text{O} & \hspace{15px} \text{dH} = -571.6 \text{ kJ} \quad (2 \times) \\
\text{2 H}_2\text{S} \rightarrow 2 \text{H}_2 + 2 \text{S} & \hspace{15px} \text{dH} = 41.2 \\
\text{SO}_2 \rightarrow \text{S} + \text{O}_2 & \hspace{15px} \text{dH} = 296.8
\end{align*}
\]

11. Given the following enthalpies (kJ) of formation,
\[
\text{H}_2\text{O}, -285.8; \text{H}_2\text{S}, -20.6; \text{SO}_2, -296.8; \text{SO}_3, 395.7; \text{CO}_2, -393.5; \text{and CO}, -110.5
\]
calculate the enthalpy change for the reaction:
\[
\text{2 CO} + \text{O}_2 \rightarrow 2 \text{CO}_2
\]
All reactants and products are in their standard states.
Hint: -566 kJ

Skill:
Evaluate the standard enthalpy of reaction from standard enthalpies of formation of reactants and products.

12. The hydration of lime, \(\text{CaO}\) (molar mass 56), gives off 65.2 kJ per mole:
\[
\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2, \hspace{15px} \text{dH} = -65.2 \text{ kJ}
\]
How much heat (in kcal) is given off when 5.0 kg of \(\text{CaO}\) is hydrated? Conversion factor: 1 kcal = 4.184 kJ.
Hint: -1391 kcal
Further interest:
\(\text{Ca(OH)_2}\) is called slaked lime. It is used in the construction industry.

13. The enthalpy of formation of \(\text{CO}_2\) from graphite is -393.5 kJ. The enthalpy of formation of diamond is +1.9 kJ. Calculate the heat of combustion of diamond to form \(\text{CO}_2\).

Hint: -395.4 kJ

Skill:
Know that \(\Delta H^\circ\) for graphite is zero (the standard state of carbon). Calculate enthalpy of combustion. Diamond is unstable with respect to graphite.

Contributors

- Chung (Peter) Chieh (Professor Emeritus, Chemistry @ University of Waterloo)