CH10087  Thermodynamics

or:

Energy Changes in Chemical Systems

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Additional Recommended Texts:

Thermodynamics of Chemical Processes  G.J. Price  OUP Primer
Basic Chemical Thermodynamics  E.B. Smith  OUP  4th Edn.

Additional sources:

Problems in Physical Chemistry (Library – various)
We are concerned with the study of *macroscopic* systems.

**Terminology and Nomenclature**
Before we start, we need to make sure that we know *precisely* what we are talking about and so need to get some definitions straight.

**Chemical systems**

*System:* the part of the Universe with which we are concerned

*Surroundings:* The rest of the Universe!

Various types of system exist:

- **isolated** systems occur where there can be no exchange of heat or matter with the surroundings.

- A **closed** system contains a fixed amount of matter but allows exchange of heat.

- **open** systems - both matter and energy can be exchanged with the surroundings.
We will mostly deal with open systems

(a). an open system  (b). a closed system

(c). an isolated system
In (c), the contents are fixed in the flask by the stopper. The vacuum flask prevents heat (energy) exchange with the surroundings. In (b) heat exchange can take place but the contents are fixed. In (a), exchange of both heat and matter with the surroundings is possible.

Changes in systems

*Precise use of symbols and terminology is vital*

The change in any property of a system is represented by the symbol $\Delta$. For any property $X$,

$$\Delta X = X\text{ (after the change)} - X\text{ (before the change)} = X_{\text{final}} - X_{\text{initial}}$$

Thus, for a system being heated from a temperature $T_1$ to $T_2$, $\Delta T = T_2 - T_1$. For a chemical reaction, $\Delta X$ would be calculated as $X(\text{products}) - X(\text{reactants})$.

If a system is heated from 20 °C to 100 °C, $\Delta T$ would be $(100 - 20) = 80$ °C. If it were cooled from 20 °C to 0 °C, $\Delta T$ would be $(0 - 20) = -20$ °C.
A reminder on Units and things

We use the absolute temperature scale so that values are measured in Kelvin.
\[ T / K = T / ^\circ C + 273.15. \]

An ideal gas:

\[ pV = n RT \]

\( p \) is the pressure when \( n \) moles of a gas occupy a volume \( V \) at temperature \( T \) (measured in Kelvin). \( R \) is the gas constant - (in S.I. units) \( 8.314 \, \text{J K}^{-1} \, \text{mol}^{-1} \).

Pressure units

a common unit was the “millimeter of mercury” or “mmHg”, named the Torr

*The standard atmosphere, 1 atm* is defined as 760 Torr.

The S.I. unit is the Pascal, \( Pa \) - the pressure when a force of 1 N acts on an area of 1 m\(^2\).

We define the bar where 1 bar = 10\(^5\) Pa.

Conversions:

- 1 Pa = 1 N m\(^{-2}\)
- 1 bar = 10\(^5\) Pa
- 1 Torr = 133.32 Pa
1 atm = 1.013 bar
= 101325 Pa
= 760 Torr

Calculate the volume occupied by 1 mole of an ideal gas at 25 °C and 1 atmosphere pressure.

\[ pV = nRT \]

\[
(101325 \text{ N m}^{-2}) (V / \text{m}^3) = (1 \text{ mol}) (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (298.15 \text{ K})
\]

\[ V = 0.02447 \text{ m}^3 = 24470 \text{ cm}^3 \]

The last equality follows since 1 m³ = 10⁶ cm³.
Energy in chemistry

Occurs in various forms: we will mainly be concerned with HEAT and WORK

In physics textbooks, energy is often defined as the capacity to do work.

From Newton's laws we define a unit for measuring energy, the Joule, J.

1 J is the work done when a force of 1 Newton acts over a distance of 1 m.

\[ 1 \text{ J} = 1 \text{ N m} = 1 \frac{\text{kg m s}^{-2}}{\text{m}} = 1 \text{ kg m}^2 \text{ s}^{-2} \]

Calculate the energy needed to lift a book weighing 1 kg from the floor to a bookshelf 2 m high.

Here the force is provided by overcoming the action of gravity on the book

\[
\text{Energy} = \text{force} \times \text{distance} \\
= (1 \text{ kg} \times 9.8 \text{ m s}^{-2}) \times (2 \text{ m}) \\
= 19.6 \text{ kg m}^2 \text{ s}^{-2} \\
= 19.6 \text{ J}
\]

Heat is the form of energy that can be transferred as a result of temperature changes.
The calorie, cal. 1 cal is the energy needed at 25 °C to heat 1 g of pure water by 1 °C. We will always use S.I. units.

The Joule and calorie are related by 1 cal = 4.181 J

We now need to quantify CHANGES in energy.

- Introduce the heat capacity, c.

The molar heat capacity is the amount of energy needed to raise the temperature of 1 mole of a substance by 1 K.

The specific heat capacity is defined in an analogous way except that it refers to 1 gram of a substance.

c therefore has units of J K$^{-1}$ mol$^{-1}$ or J K$^{-1}$ g$^{-1}$.

If q Joules of heat are added to a system containing n mol or m grams of a substance and the temperature is raised from $T_1$ to $T_2$ then,

$$q = m \ c_s \ \Delta T = n \ c_m \ \Delta T$$

where $\Delta T = T_2 - T_1$. 
The heat capacity of liquid water is 4.18 J K$^{-1}$ g$^{-1}$. Calculate the energy required to heat 1 mole of water from 25 to 90 °C.

Since the value is quoted per gram, it must be the specific heat capacity. Taking the molar mass of water as 18 g mol$^{-1}$,

$$ q / J = (1 \text{ mol} \times 18 \text{ g mol}^{-1}) \times (4.18 \text{ J K}^{-1} \text{ g}^{-1}) \times (363.15 - 298.15 \text{ K})$$

$$ = 4890.6 \text{ J} = 4.89 \text{ kJ}$$

Note that the temperatures were converted from degrees Celsius to Kelvin. Even though this was not necessary in this particular problem, it is a good habit to always use K as the units for temperature.

Later, we will see that the value of the heat capacity will vary depending on the conditions under which it is measured and it also depends on temperature. However, this will suffice for present purposes.

**Quantifying changes of work**

**A simple example:** a reaction forms a gas inside a cylinder (with a frictionless piston!) - performed isothermally.
The piston moves a distance $dx$ against the external pressure, $p_{\text{ext}}$, changing the volume from $V_{\text{initial}}$ to $V_{\text{final}}$.

The force acting on the piston can be calculated since

$$\text{pressure} = \frac{\text{force}}{\text{area}} \quad \text{or} \quad F = p_{\text{ext}} \pi r^2$$

work done = force $\times$ distance moved

$$dw = p_{\text{ext}} \pi r^2 (-dx) = -p_{\text{ext}} \, dV$$

dw is therefore the work done when the gas expands through a volume $dV$ against a pressure, $p_{\text{ext}}$.

Since $V$ is continually changing, we need to integrate between the initial and final volume

$$w = -p_{\text{ext}} \int_{V_{\text{initial}}}^{V_{\text{final}}} \, dV = -p_{\text{ext}} \left( V_{\text{final}} - V_{\text{initial}} \right)$$