

2106NSC

Physical & Analytical Chemistry

Thermodynamics 2

Revision of some basic concepts
in Fundamental Thermodynamics

Equations of state

The physical state of a system is described by its physical properties.

For example, the state of a pure gas is specified by giving its volume (measured in liter), the amount (measured in moles), pressure (measured in Pa) and temperature (measured in K).

Experimentally, it has been found that if you specify 3 of these 4 variables, the 4th one will have a discrete value.

This means that there exists an equation that relates 3 of the variables to the 4th.

Such an equation is called an equation of state.

$$p = f(T, V, n) \quad V = f(T, p, n) \quad T = f(p, V, n) \quad n = f(T, V, p)$$

Equations of state

The ideal gas equation is an example of an equation of state:

$$p \cdot V = n \cdot R \cdot T$$

$$p = n \cdot R \cdot T / V$$

$$V = n \cdot R \cdot T / p$$

$$n = p \cdot V / (R \cdot T)$$

$$T = p \cdot V / (n \cdot R)$$

Energy

Energy describes the capacity of a system to do work.

Energy is a **state function** and an **extensive property** (depends on the amount of substance).

Units

SI unit: Joule

other common units : calorie

$$[E] = 1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2} = 1 \text{ V C}$$

$$1 \text{ cal} = 4.184 \text{ J}$$

Various types

kinetic energy

$$E_{\text{kin}} = \frac{1}{2} \cdot m \cdot v^2 \text{ (Newtonian mechanics)}$$

potential energy

$$E_{\text{pot}} = m \cdot g \cdot h ; g = 9.81 \text{ m s}^{-2} \text{ (Newtonian mechanics)}$$

chemical energy

energy present in the bonds between atoms and molecules

thermal energy

due to the vibration and movement of the atoms and molecules in a substance

electric energy

potential difference between two half-cells with electron conducting link

osmotic energy

difference in salt concentration in two half cells separated by a semi-permeable membrane

The total energy of a system is its **internal energy U** .

Work

Work is done when an object is moved against an opposing force (e.g. electrical work - electrons moving; work of expansion/compression - particles moving).

Work results in a change of the energy of the system : $U = Q + W$

Work is a **path function**, i.e. it depends on how the process occurs.

The 1st Law of Thermodynamics

The internal energy of an isolated system is constant:

$$\Delta U = \Delta Q + \Delta W$$

Any change in the internal energy of a system is a result of work done on the system (ΔW) and heat transferred to the system (ΔQ).

Work of expansion/contraction

The amount of work to be done for contraction or expansion will depend on the change of the volume of the system ($\Delta V = V_{\text{final}} - V_{\text{initial}}$) and the surrounding restrictions presented by the external pressure p_{ext} .

Macroscopically: $\Delta W = - p_{\text{ext}} \cdot \Delta V$

If we consider very small changes, we need to move from the macroscopic difference (Δ) to a differential (d):

$$dW = - p_{\text{ext}} \cdot dV$$

From a differential, one can calculate the total amount by integration:

$$W = - \int_{V_{\text{initial}}}^{V_{\text{final}}} p_{\text{ext}} \cdot dV = - p_{\text{ext}} \cdot (V_{\text{final}} - V_{\text{initial}}) = - p_{\text{ext}} \cdot \Delta V$$

Work of expansion/contraction

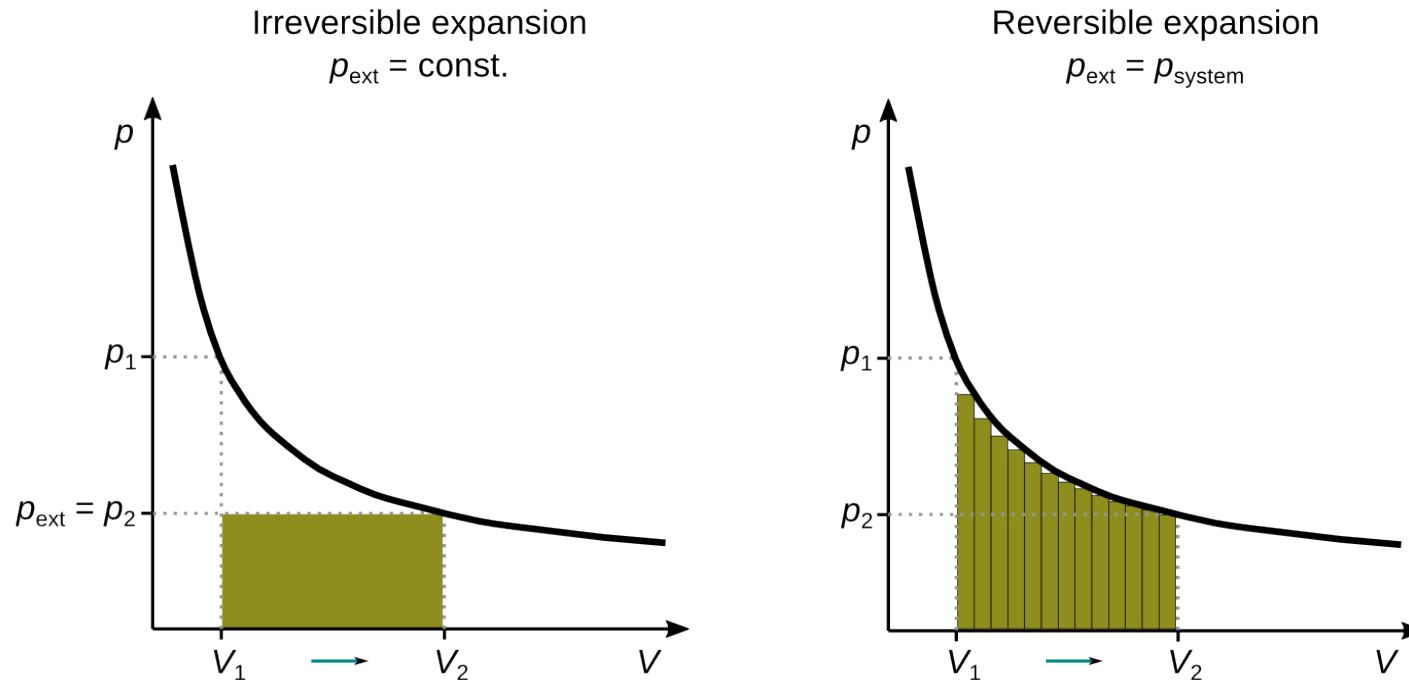
$$W = - \int_{V_{\text{initial}}}^{V_{\text{final}}} p_{\text{ext}} dV$$

If the external pressure is zero (free expansion possible, vacuum), this expression yields $W = 0$, so there is no work done!

If the external pressure is gradually changed so that the internal and external pressure remain the same at all times, expansion/contraction is carried out reversibly, so

$$W = W_{\text{rev}} = - \int_{V_{\text{initial}}}^{V_{\text{final}}} p dV$$

Work of expansion/contraction



It is clear that the most work will be done when the process is carried out so that the external pressure is as close as possible to the internal pressure at all times. In the limiting case, when the internal and external pressures are equal, changes will occur infinitesimally slowly - the system will be at equilibrium with the surroundings at all times - and the process is said to be reversible. More generally, **the magnitude of the work is maximised in a reversible process.**

Heat

When energy changes as a result of a temperature difference between the system and its surroundings, we say there is a flow of heat (ΔQ).

If there is no flow of heat during a process, this is called an **adiabatic** process.

The total change in energy is due to heat transfer and work done by/on the system :

$$\Delta U = U_{\text{final}} - U_{\text{initial}} = \Delta W + \Delta Q$$

Heat, work, energy change and reversibility

Heat and work are path functions, i.e. they depend on the way how the change occurs.

In contrast, energy is a state function.

If the system is at equilibrium with its surroundings at all times, the process of exchange is said to be reversible.

The magnitude of the work is maximised in a reversible process.

Heat capacity

The change in the internal energy of a substance when the temperature is raised is described by the heat capacity at constant volume

$$C_V = \left(\frac{\delta U}{\delta T} \right)_V$$

At constant volume: $dU = C_V \cdot dT$

the inner energy of a system varies linearly with the temperature, correlated by the heat capacity C_V as a factor.

If the heat capacity does not change over the temperature range considered, then at constant volume: $\Delta U = C_V \cdot \Delta T = Q_V$

This provides an easy way to measure the heat capacity of a substance: measure the heat provided to the system (e.g. electrically) and observe the temperature change. This is done with an adiabatic bomb calorimeter.

Heat capacity

The heat capacity is **extensive**: it increases with the amount of substance.

The corresponding **intensive** properties are:

- molar heat capacity heat capacity of 1 mole of substance
- specific heat heat capacity of 1 g of substance

Enthalpy

Consider heat is transferred into an open container filled with water. The water will expand its volume as it gets 'hotter', and pushes back the atmosphere.

The energy of the system is not simply $\Delta U = \Delta Q$, because it simultaneously loses energy due to the work it does by pushing back the atmosphere.

The quantity that takes into account the simultaneous loss of energy by contraction/expansion is called enthalpy:

$$H = U + p \cdot V$$

Under constant external pressure, the enthalpy change is thus the same as the transferred heat:

$$\Delta H = \Delta Q, \text{ if } p = \text{const. and no other work done.}$$

Enthalpy

Enthalpy can be measured calorimetrically, where the change in temperature is monitored due to a change at constant pressure. The instrument used is called a differential scanning calorimeter (DSC).

If a reaction (process) involves only liquids and solids, the product $p \cdot V$ is very small, therefore $H \approx U$, and ΔU can be measured.

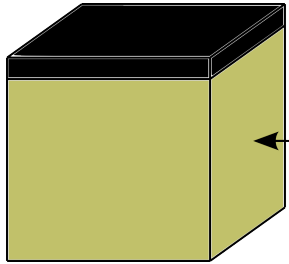
The enthalpy variation of a system with temperature is described by the heat capacity at constant pressure:

$$C_p = \left(\frac{\delta H}{\delta T} \right)_p$$

Relationship between heat capacities for an ideal gas:

$$C_p - C_V = n \cdot R$$

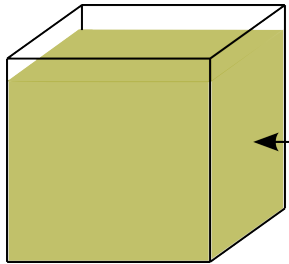
Internal energy and enthalpy



$$\Delta U = \Delta Q + \Delta W ; \Delta W = 0 \quad \Rightarrow \quad \Delta U = \Delta Q$$

Since the container is closed, the system cannot expand and thus not do any work; the internal energy equals the transferred heat.

$$H = U + p \cdot V \quad \Rightarrow \quad \Delta H = \Delta U + p \cdot \Delta V + V \cdot \Delta p$$
$$\Delta H = \Delta Q + p \cdot 0 + V \cdot \Delta p$$
$$\Delta H = \Delta Q + V \cdot \Delta p$$



$$\Delta U = \Delta Q + \Delta W ; \Delta W = -p_{\text{ext}} \cdot \Delta V \quad \Rightarrow \quad \Delta U = \Delta Q - p_{\text{ext}} \cdot \Delta V$$

In case of the open container, the system will expand and thus conduct work against the outside pressure.

$$H = U + p \cdot V \quad \Rightarrow \quad \Delta H = \Delta U + p \cdot \Delta V + V \cdot \Delta p$$
$$\Delta H = \Delta Q - p \cdot \Delta V + p \cdot \Delta V + V \cdot \Delta p$$
$$\Delta H = \Delta Q - p \cdot \Delta V + p \cdot \Delta V + V \cdot 0$$
$$\Delta H = \Delta Q$$

Suggested Reading

Hofmann, A (2016) *Introduction to Physical Chemistry*, 2nd Edition, Structural Chemistry Program, Griffith University.
Sections II.1.2 – II.1.9

Atkins, PW & de Paula, J (2010) *Physical Chemistry*, 9th Edition, Oxford University Press.
Sections 2.1 – 2.6 (pp. 44-64)