First Law of Thermodynamics

Chapter 2
Conservation of Energy

Concept of Internal Energy, \( U \)

Internal energy is the sum of the kinetic and potential energies of the particles that make up the system.

At molecular level, contributors to the internal energy, \( U \) are:

- translational energy of the molecules.
- energy in the form of molecular vibrations and rotations.
- potential energy of the constituents of the system due to the environmental effects (intra).
- energy stored in the form of chemical bonds that can be released through a chemical reaction.
- potential energy of interaction between molecules (inter).

Translational
whole atom or molecule changes its location in three dimensional space

Rotational
whole molecule spins around an axis in three dimensional space

Vibrational \( \leftrightarrow \) Motion within molecule
motion that changes the shape of the molecule – stretching, bending, and rotation of bonds

All types of energy of molecules, except translational energy are quantized.

\[
f(v) = \sqrt{\left( \frac{m}{2nkT} \right)^3} 4\pi v^2 e^{-\frac{m v^2}{2kT}}, \quad KE = \frac{1}{2} m \left\langle v^2 \right\rangle
\]
The first law of thermodynamics

The first law of thermodynamics states that energy can be neither created nor be destroyed, if the energies of both the system and the surroundings are taken into account.

\[ U_{\text{final}} = U_{\text{initial}} + U_{\text{sur}} \]

\[ \Delta U_{\text{total}} = \Delta U_{\text{system}} + \Delta U_{\text{surroundings}} = 0 \]

\[ \Delta U_{\text{sys}} = -\Delta U_{\text{sur}} \]

The internal energy \( U \) of an isolated system is constant, i.e. \( \Delta U_{\text{sys}} = 0 \).

Simple processes:

The simplest processes; one of P, V or T remains constant.

A constant temperature process is referred to as isothermal.
A constant pressure process is referred to as isobaric.
A constant temperature process is referred to as isochoric.

Work: mechanical work (P-V) \( w \):

P-V work is the energy transfer across the boundary between the system and the surroundings due to a force acting through a distance (from expansions (-ve) and contractions (+ve) of system volume).

Work is performed by other ways too, e.g. electrical, sonar,

Changing \( U \):

In a closed system in which no chemical reactions or phase changes occur; heat, work, or a combination of both is the means to change \( U \).

In such a system the flow of heat, \( q \), and/or work, \( w \), across the boundary between the system and surroundings during a process which change \( U \) of the system \( \Delta U \); 

\[ \Delta U = q + w \]

Heat into the system, \( q > 0 \)
Work done on the system, \( w > 0 \)

Work: \( w \) (isothermal process) on the system (+ve):

\[ w = \int_{x_i}^{x_f} \mathbf{F} \cdot dx \]

\[ w = \frac{-1}{\gamma} \int P dV \]

\( w > 0 \), on system-contraction
\( w < 0 \), by system-expansion
Heat:

Heat is the energy transfer across the boundary between the system and the surroundings (flows from high temperature to low temperature) due to the temperature difference between them.

Surroundings:

Everything other than the system is surroundings.

As a practical matter for a given situation only the immediate region that can interact with the system is the (effective) surrounding.

Molecular Level Perspective:

In the final analysis matter has to be viewed in terms of their existence of entities as atoms, molecules, macromolecules…

At molecular level the energy an entity can acquire is quantized. Allowed energies of entities are well defined, $\varepsilon_1$, $\varepsilon_2$, $\varepsilon_3$, $\varepsilon_4$, …

All the molecules in a system do not have the same energy. There is a distribution of energies among them at a given temperature.

The relative probability of a molecule in allowed energy states $\varepsilon_1$ and $\varepsilon_2$ ($>\varepsilon_1$) is given by:

$$\frac{n_2}{n_1} = e^{-\frac{(\varepsilon_2 - \varepsilon_1)}{kT}} \quad \text{as} \quad (\varepsilon_2 - \varepsilon_1) \to \frac{n_2}{n_1} \to$$

Smaller energy gaps Bigger energy gaps

Low $T$ High $T$
Heat Capacity, \( C \)

Flow of heat in/out of matter (system) results in a temperature change of the matter in the system. The amount of heat (strictly speaking energy) required \( C \), to change the temperature is defined as the heat capacity

\[
C = \lim_{\Delta T \to 0} \frac{q}{T_f - T_i}
\]

\[
C = \frac{dq}{dT}
\]

\( C \) depends on the material - SI unit; J K\(^{-1}\).

per mole of material, \( C_m \) - SI unit; J K\(^{-1}\) mol\(^{-1}\).

Heat capacity depends on the experimental conditions as well. Constant P heat capacity, \( C_p \), is different from constant V heat capacity, \( C_V \).

Molecular view of \( C \)

Heat exchanging with matter changes the temperature, and therefore the populations in the energy levels change. The energy levels in a molecule in general is the sum of different (energetic degrees of freedom) types of energies;

\[
E_{\text{tot}} = E_{\text{tr}} + E_{\text{rot}} + E_{\text{vib}} + E_{\text{elec}} + \ldots
\]

Molecules can gain/lose energy from/to other molecules via molecular collisions.

Energy levels – comparison

Equation of energy states: each quadratic term in the classical expression for the energy contributes \( \frac{1}{2}RT \) (J mol\(^{-1}\) K\(^{-1}\)) the average energy.

For instance, the translational motion of an atom or molecule has three degrees of freedom (number of ways of absorbing energy), corresponding to the x, y and z components of its momentum.

Since these components of momenta appear quadratically in the kinetic energy, every atom has an average kinetic energy of \( (3/2)RT \) in thermal equilibrium.

The contribution to heat capacity $C_{V_m}$ for a gas at a temperature of $T$ not much lower than 300 K is $R/2$ for each translation and rotational degree of freedom, where $R$ is the ideal gas constant.

Each vibrational degree of freedom for which the relation $\Delta E/kt < 0.1$ (is active) contributes $R$ to $C_{V_m}$.

If $\Delta E/kt > 10$ (is inactive) such degree of freedom does not contribute to $C_{V_m}$.

For $10 > \Delta E/kt > 0.1$, the degree of freedom contributes partially to $C_{V_m}$.

*Each active degree of freedom contribute to the heat capacity.*

$C_{V_m}$ for gases:

Monoatomic gases: $E_{tot} = E_{tr}$

$$C_{V_m} = 3(R/2) \text{ J mol}^{-1} \text{ K}^{-1}$$

Polyatomic gases with rotations active: $E_{tot} = E_{tr} + E_{rot}$

$$C_{V_m} = 3(R/2) + 2(R/2) - \text{ linear}$$

$$C_{V_m} = 3(R/2) + 3(R/2) - \text{ non linear}$$

Polyatomic gases with rotations and vibrations active (upper limit):

$$E_{tot} = E_{tr} + E_{rot} + E_{vib}$$

$$C_{V_m} = 3(R/2) + 2(3n-5)(R/2) - \text{ linear}$$

$$C_{V_m} = 3(R/2) + 3(3n-6)(R/2) - \text{ non linear}$$

Calculation of $q_V$:

$$C_p = \frac{dq_V}{dT} \implies q_V = \int_{T_{sys,i}}^{T_{sys,f}} C_p \,dT$$

Heat for constant pressure processes (gases):

Under constant pressure changing temperature would change volume of the gas. This involves pushing or pulling of ‘surrounding’, thus involves mechanical work.

The energy (heat) required to change the temperature, $C_{p_m}$, for constant pressure processes are different from $C_{V_m}$.

$$q_p = \int_{T_{sys,i}}^{T_{sys,f}} C_p^{ext} \,dT = - \int_{T_{sys,i}}^{T_{sys,f}} C_p^{sur} \,dT$$
For gases $C_p > C_V$ because energy is needed to effect volume changes.

\[ C_p - C_V = nR \quad \text{i.e.} \quad C_{pm} - C_{vm} = R \]

Borrowed Chapter 3

State functions and path functions:

\[ \Delta U = q + w \]

\[ dU = \delta q + \delta w \]

Any quantity that does not depend on the path it takes to move from stage 1 to stage 2 is a state function. All thermodynamic quantities are state functions. State of a single phase of fixed composition is characterized by any two of $P$, $V$ and $T$.

Any quantity that depend on the path it takes to move from stage 1 to stage 2 is a path function; $q$ and $w$ are path functions.

A state function describes the current state of a system.

How the system came to be in that particular state is of no consequence.

The following are state functions:

- Pressure, $P$
- Volume, $V$
- Temperature, $T$
- Mass, $m$
- Quantity, $n$
- Internal Energy, $U$
- Enthalpy, $H$
- Entropy, $S$
- Gibbs Energy, $G$

The overall change for a cyclic process of a state function is zero.

\[ \Delta U = \int_{i}^{f} dU = U_f - U_i \]

\[ \oint dU = 0 \quad \text{cyclic path} \]
Thermodynamics applies to systems in internal equilibrium. It implies any change done must be performed giving sufficient time to achieve equilibrium internally and with the surroundings; rate of change - slow – very slow; quasi-static process.

We deal with quasi-static processes which are reversible.

Reversible process: A reversible process is a process where the effects of following a thermodynamic path can be undone by exactly reversing the path. It is a process that is always at equilibrium even when undergoing a change. Ideally the composition throughout the system must be homogeneous.

Reversible process:

Therefore the no gradients, currents or Eddys exist. To prevent all in-homogeneities, a reversible process must be carried out infinitely slowly.

A truly reversible processes is non-existent. However, many systems are approximately reversible. Assuming reversible processes facilitates calculations of various thermodynamic state functions.

Fact: Maximum work is achieved from the system during a reversible expansion and vice versa.

**P-V isotherms do not cross.**

\[ P = \frac{nRT}{V} \]

Isothermal process

All points on the surface correspond to all possible P, V and T values (equilibrium state) of 1mol of an ideal gas.
Reversible P-V changes of an ideal gas (isothermal):

\[ PV = nRT = \text{constant} \]

Maximum work is involved during a reversible expansion (or compression).

Reversible process follows the IGE.

\[ w = -nRT \ln \frac{V_f}{V_i} \]
\[ w_{\text{expansion}} = -nRT \ln \frac{V_f}{V_i} \]
\[ w_{\text{compression}} = -nRT \ln \frac{V_i}{V_f} \]

\[ w_{\text{total}} = 0; \quad q_{\text{total}} = 0 \]

For the irreversible process, P-V work

\[ w = -P_{\text{net}} \Delta V \]
\[ |w| = P - V \text{ indicator diagram plot area} \]
For the cyclic irreversible process, P-V work

\[ w = -P_{cu} \Delta V \]

\[ |w| = P - V \text{ plot area} \]

\[ w = - \sum_{cycle} P_{cu} \Delta V \]

For P-V work \( w_{irrev} < w_{rev} \).

Example Problem 2.4 p.32

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In this example, 2.00 mol of an ideal gas undergoes isothermal expansion along three different paths: (1) reversible expansion from \( P_1 = 250 \text{ bar} \) and \( V_1 = 4.90 \text{ L} \), to \( P_2 = 4.50 \text{ bar} \), (2) a single-step irreversible expansion against a constant external pressure of 4.50 bar, and (3) a two-step irreversible expansion consisting initially of an expansion against a constant external pressure of 11.0 bar until \( P = P_{cu} \), followed by an expansion against a constant external pressure of 4.90 bar until \( P = P_{cu} \).

Calculate the work for each of these processes. For which of the irreversible processes is the magnitude of the work greater?
Solution
The processes are depicted in the following indicator diagram:

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The magnitude of the work is greater for the two-step process than for the single-step process, but less than that for the reversible process.

For P-V work $|w_{\text{irrev}}| < |w_{\text{rev}}|$.

Expansion

Smaller steps (slower) process closer to reversible.

Maximum work is involved during a reversible expansion (or compression).

Compression

Smaller steps (slow) process closer to reversible.

We first calculate the constant temperature at which the process is carried out, the final volume, and the intermediate volume in the two-step expansion:

$T = \frac{pV_i}{nN} = \frac{25.0 \text{ bar} \times 4.50 \text{ L}}{8.314 \times 10^{-5} \text{ L bar mol}^{-1} \text{ K}^{-1} \times 2.00 \text{ mol}} = 677 \text{ K}$

$V_f = \frac{pF}{p_f} = \frac{8.314 \times 10^{-2} \text{ L bar mol}^{-1} \text{ K}^{-1} \times 2.00 \text{ mol} \times 677 \text{ K}}{4.50 \text{ bar}} = 25.0 \text{ L}$

$V_{\text{int}} = \frac{pF}{p_{f,k}} = \frac{8.314 \times 10^{-2} \text{ L bar mol}^{-1} \text{ K}^{-1} \times 2.00 \text{ mol} \times 677 \text{ K}}{11.0 \text{ bar}} = 10.5 \text{ L}$

Use Boyle’s Law, easier!!
Determination of $\Delta U$

$$\Delta U = q + w = q - \int P_{\text{external}} dV$$

If $dV = 0$; \hspace{0.5cm} $\Delta U = q = q_v$

$$\Delta U = q_v$$

Perform the process under constant volume, and measure the heat flow, $q_v$ associated.

**Enthalpy:**

Processes performed under constant pressure $dU$ would be:

$$dU = dq_v - P_{\text{external}} dV$$

$$\int dU = q_v - \int P dV = q_v - P \int dV$$

$$U_f - U_i = q_v - P \left(V_f - V_i\right) \quad \text{and} \quad P_f = P_i$$

$$q_v = U_f - U_i + P_f V_f - P V_i$$

$$H = U + PV$$ \hspace{0.5cm} \text{Enthalpy}$$

$$q_v = H_f - H_i = \Delta H$$

$$\Delta H = q_v$$

**Calculation of $q$, $w$, $\Delta U$ and $\Delta H$ for ideal gases:**

Needed: equation of state, initial state, final state and the path taken.

$$\Delta U = q_v = \int C_v dT \quad \text{U function of } T$$

$$\Delta H = \Delta U(T) + \Delta(PV) = \Delta U(T) + \Delta(nRT) \quad \text{H function of } T$$

$$= q_v = C_v \Delta T$$

$$\Delta H = q_v = C_v \Delta T$$

$$w = -\int P_{\text{external}} dV = -\int \frac{nRT}{V} dV$$

**Note:**

Isothermal process: \hspace{0.5cm} $\Delta H = \Delta U = 0$

Adiabatic process: \hspace{0.5cm} $q = 0$ \hspace{0.5cm} definition

P-V work, constant volume: \hspace{0.5cm} $w = 0$
Reversible Adiabatic Expansion/Compression: Ideal Gas

Consider the adiabatic expansion of an ideal gas. Because \( q = 0 \), the first law takes the form:

\[
\Delta U = w = - \int P_{\text{external}} \, dV = \int C_v \, dT
\]

\[
C_v \, dT = - nRT \frac{dV}{V}
\]

\[
C_v \, \frac{dT}{T} = - nR \frac{dV}{V}
\]

\[
\Rightarrow C_v \ln \frac{T_f}{T_i} = - nR \ln \frac{V_f}{V_i}
\]

Two systems containing 1 mol of \( \text{N}_2 \) have the same \( P \) and \( V \) values at 1 atm.

Isothermal:
\( P > 1 \rightarrow q < 0 \) to keep \( T \) const.
\( P < 1 \rightarrow q > 0 \)

Adiabatic: \( q = 0 \)
\( P > 1 \rightarrow T \) increase, \( P_{\text{ad}} > P_{\text{iso}} \)
\( P < 1 \rightarrow T \) decrease, \( P_{\text{ad}} < P_{\text{iso}} \)

\[
C_v \ln \frac{T_f}{T_i} = - nR \ln \frac{V_f}{V_i}
\]

\[
C_v \ln \frac{T_f}{T_i} = -(C_p - C_v) \ln \frac{V_f}{V_i}
\]

\[
\ln \frac{T_f}{T_i} = \frac{(C_p - C_v)}{C_v} \ln \frac{V_f}{V_i}
\]

\[
= -(\gamma - 1) \ln \frac{V_f}{V_i}
\]

where \( \gamma = \frac{C_p}{C_v} \)

\[
\ln \frac{T_f}{T_i} = \ln \left(\frac{V_f}{V_i}\right)^{(1-\gamma)}
\]

\[
\ln \frac{T_f}{T_i} = \frac{P_fV_f}{P_iV_i} = \left(\frac{V_f}{V_i}\right)^{(1-\gamma)}
\]

\[
P_fV_f \left(\frac{V_f}{V_i}\right)^{(1-\gamma)} = 1
\]

\[
P_fV_f = PV_i^{\gamma}
\]