Properties of Gases (Chapter 2)

Why gases? Gas described in terms of few variables (temperature, pressure, volume, composition). Thermodynamic properties easy to describe.

Definitions:

**System**: What we are interested in (cell, container of gas, etc.)

**Surroundings**: The rest of the universe.

Three kinds of systems: **Open, Closed and Isolated**.

**Open system**: Exchanges mass and energy with surroundings.

**Closed system**: Exchanges energy (not mass) with surroundings.

**Isolated system**: Exchanges neither energy nor mass with surroundings.
Properties of Gases (Chapter 2)

**State of System**: Variables needed to describe system. For gases these are temperature (T), pressure (p), volume (V) & composition.

**Equation of state**: Relates variables to one another.

**Ideal gas**: \[ pV = nRT \]

- \( n = \) number of moles
- \( R = \) gas constant
Properties of Gases (Chapter 2)

**Extensive properties:** Properties that are proportional to amount of material in system. Examples: Mass, volume, energy.

**Intensive properties:** Do not depend on amount of material in system. Examples: pressure, temperature, density.

Intensive property often ratio of extensive properties. Examples:

\[
\text{density} = \frac{\text{mass}}{\text{volume}}
\]

\[
\text{pressure} = \frac{\text{force}}{\text{area}}.
\]
Boyle’s Law

Gas at volume $V'$ and pressure $p'$

**Gas:**
$V', p'$

Expand container at constant temperature to new volume $V''$:
get new pressure $p'' < p'$

**Gas:**
$V'', p''$

Volume inversely proportional to pressure:

**Boyle’s Law:**

$V \propto \frac{1}{p}$

or

$pV = \text{constant}$
**Charles’ and Gay Lussac’s Law**

- All isobars meet at \( T = -273.15 \, ^\circ C \)
- \( T = -273.15 \, ^\circ C \) is lowest possible temperature, “absolute zero”.
- Define new unit of temperature, Kelvin (K):
  \[ T(K) = T(\, ^\circ C) + 273.15 \]

**Volume proportional to temperature:**

**Charles’ Law**

\[ V \propto T \]

or

\[ V/T = \text{constant} \]
Charles' and Gay Lussac's Law

Volume proportional to temperature at constant pressure:

\[ V \propto T \quad \text{(constant p)} \]

or

\[ \frac{V}{T} = \text{constant} \]

Also:

Pressure proportional to temperature at constant volume:

\[ p \propto T \quad \text{(constant V)} \]

or

\[ \frac{p}{T} = \text{constant} \]
Avogadro’s Law

Equal volumes of gases at the same $T$ and $p$ contain the same number of molecules:

$$ V \propto n \quad (\text{constant } T, p) $$

or

$$ V/n = \text{constant} $$

$n = \text{number of moles}$

$1 \text{ mole} = 6.02 \times 10^{23} \text{ molecules}$
Ideal gas equation of state

\[ V \propto \frac{1}{p} \quad \text{(constant } T, n) \quad \text{Boyle's Law} \]
\[ V \propto T \quad \text{(constant } p, n) \quad \text{Charles' Law} \]
\[ V \propto n \quad \text{(constant } T, p) \quad \text{Avogadro's Law} \]

Putting the laws together:

\[ V \propto \frac{nT}{p} \]
\[ \text{or} \]
\[ V = \frac{RnT}{p} \quad (R = \text{“gas constant”}) \]
Ideal gas equation of state

\[ V = \frac{RnT}{p} \quad (R = \text{“gas constant”}) \]

or

\[ pV = nRT \]

What is \( R \)?

Under standard conditions, \( p = 1 \text{ atm}, T = 273.15 \text{ K} \),
1 mole of ideal gas occupies 22.414 L:

\[ R = \frac{pV}{nT} = \frac{(1 \text{ atm})(22.414 \text{ L})}{(1 \text{ mol})(273.15 \text{ K})} \]

\[ R = 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \]
Example: Air entering lungs ends up in alveoli. Average radius of alveoli = 0.0050 cm and air contains 14 mole % $O_2$. What is the number of $O_2$ molecules in an alveolus if $p = 1$ atm, $T = 37 \, ^\circ C$?
Dalton’s law of partial pressure:

Usually we have a mixture of components in a gas. Assume gas has 2 components:

\[ p_T = \text{total pressure} = p_1 + p_2 \]

- \( p_1 = “\text{partial pressure}” \) of component 1
- \( p_1 = \text{pressure exerted by component 1 if we remove component 2} \)

\[ p_1 V = n_1 RT, \quad p_2 V = n_2 RT, \quad p_T V = n_T RT \]

- \( n_1 = \text{number of moles of component 1} \)
- \( n_T = n_1 + n_2 \)

Then:

\[ p_1 = x_1 p_T \]

\[ x_1 = n_1/n_T = \text{mole fraction of component 1} \]
Thermodynamics: First Law (Chapter 3)

First law addresses conservation of energy and different forms of energy:

**Work** (useful energy)  **Heat** (not useful energy)

Mechanical work = - force x distance  
= - mass x acceleration x distance

Example: Isothermal expansion of a gas

Change in height:  \( \Delta h = h_2 - h_1 \)
Thermodynamics: First Law (Chapter 3)

Mechanical work = - force x distance
= - mass x acceleration x distance

Example: Isothermal expansion of a gas

height: \( h_1 \)  \qquad h_2 \]

Change in height:
\( \Delta h = h_2 - h_1 \)

= distance mass moved

Work = - mass x acceleration x distance = \(-mg \Delta h\)

\( g = \) acceleration due to gravity = 9.81 m/s\(^2\)

Note: work done by system on surroundings is negative.
Work

height: $h_1$ | $h_2$

Change in height:

$\Delta h = h_2 - h_1$

= distance mass moved

work = - mass $\times$ acceleration $\times$ distance = $-mg \Delta h$

$g = \text{acceleration due to gravity} = 9.81 \text{ m/s}^2$

Pressure opposing expansion: $P_{\text{ex}} = \text{(force} \div \text{area)} = \frac{mg}{A}$

$A = \text{surface area of piston}$

work = $-mg \Delta h = -P_{\text{ex}} A \Delta h = -P_{\text{ex}} \Delta V$

$\Delta V = \text{change in volume} = A \Delta h$
**Work**

**Change in height:**

\[ \Delta h = h_2 - h_1 \]

= distance mass moved

**W = work = \(-P_{ex}\) \(\Delta V\)**

\[ \Delta V = \text{change in volume} \]

work = shaded area

\[ P_{ex} = P_2 \]

\[ \Delta V = V_2 - V_1 \]
Work

Many small steps

height: $h_1 \rightarrow h_2$

Integral: sum over many small steps

Work obtained as sum over small changes in V.

$$w = \text{work} = -\int_{V_1}^{V_2} P_{\text{ex}} \, dV$$

At each step of expansion, $P_{\text{ex}} \approx P$ inside container

$P$ inside container = $nRT/V$ \quad --> \quad w = -\int_{V_1}^{V_2} P_{\text{ex}} \, dV = -\int_{V_1}^{V_2} (nRT/V) \, dV$
Work

height: \( h_1 \) \[ \rightarrow \] \( h_2 \)

\[
\begin{align*}
V_2 &= \int \left( \frac{nRT}{V} \right) dV = -nRT \ln \left( \frac{V_2}{V_1} \right) \\
Boyle's \ law: \quad pV &= \text{constant} \quad \rightarrow \quad p_1V_1 = p_2V_2 \\
Then: \quad w &= -nRT \ln \left( \frac{V_2}{V_1} \right) = -nRT \ln \left( \frac{p_1}{p_2} \right)
\end{align*}
\]

Maximum work: change system in many small steps (reversible process) rather than a few big steps (irreversible process).
Example: 0.850 mol of ideal gas initially at $p = 15.0$ atm and $T = 300$ K expands isothermally until $p = 1.00$ atm. Calculate the work done if expansion is carried out

(a) against vacuum

(b) against constant $p_{ex} = 1.00$ atm

(c) reversibly
Work

One-step, irreversible process:

Many-step, reversible process:

\[ w = \text{work} = -P_{\text{ex}} \Delta V \]

\[ w = -nRT \ln \left( \frac{V_2}{V_1} \right) \]

More useful energy from process involving many steps rather than just one big step.
**State function**: property that depends only on state of the system. If the state changes, the change in value of the state function depends only on initial and final states, not on the path to get there.

Example: Volume is a state function.

Change in volume, $\Delta V = V_2 - V_1$, independent of how the system changed from state 1 to state 2.

**Work is not a state function**. Work depends on how the system changes from state 1 to state 2.
Heat

Heat: transfer of energy between two objects at different temperatures.

Heat, \( q \), flows from hot to cold object until temperature of both is equal.

Heat, like work, is not a state function. The amount of heat, \( q \), transferred depends on how the hot object cools.
First law of Thermodynamics

Energy can be converted from one form to another, but not created or destroyed.

\[ E_{\text{universe}} = E_{\text{system}} + E_{\text{surroundings}} \]

Energy of universe does not change:

\[ \Delta E_{\text{universe}} = \Delta E_{\text{system}} + \Delta E_{\text{surroundings}} = 0 \]

Therefore:

\[ \Delta E_{\text{system}} = -\Delta E_{\text{surroundings}} \]

In chemistry, energy of system called internal energy, U.

Change in internal energy to go from state 1 \( \rightarrow \) 2, \( \Delta U = U_2 - U_1 \)

\[ \Delta U = q + w \]

q, w are path dependent, but \( \Delta U \) is not path dependent. (U is state function.)
First law of Thermodynamics

Heat and work sign conventions:

<table>
<thead>
<tr>
<th>Process</th>
<th>Sign</th>
</tr>
</thead>
<tbody>
<tr>
<td>Work by system on surroundings</td>
<td>-</td>
</tr>
<tr>
<td>on system by surroundings</td>
<td>+</td>
</tr>
<tr>
<td>Heat absorbed by system from surroundings (endothermic)</td>
<td>+</td>
</tr>
<tr>
<td>emitted by system to surroundings (exothermic)</td>
<td>-</td>
</tr>
</tbody>
</table>
First Law of Thermodynamics

Change in system’s internal energy: \[ \Delta U = U_2 - U_1 = q + w \]

\[ q = \text{heat} \quad \quad w = \text{work} \]

Example: Irreversible gas expansion at constant pressure:

\[ w = -p \Delta V \quad \rightarrow \quad \Delta U = q - p \Delta V \]

Experiments often done at constant pressure.

\[ q_p = \text{heat transferred at constant pressure} \]

Then:

\[ \Delta U = q + w = q_p - p \Delta V \]
First Law of Thermodynamics

Enthalpy: \[ H = U + pV \]

At constant pressure:

\[ \Delta U = q_p - p \Delta V \quad \rightarrow \quad U_2 - U_1 = q_p - p (V_2 - V_1) \]

Rearranging:

\[ q_p = U_2 + p V_2 - (U_1 + p V_1) \]

Also:

\[ \Delta H = H_2 - H_1 = U_2 + p_2 V_2 - (U_1 + p_1 V_1) \]

Therefore:

\[ \Delta H = q_p \quad \text{if} \quad p = p_2 = p_1 \]

Note: \text{H} is state function, since \text{p}, \text{V}, \text{U} are all state functions.
How does $\Delta U$ compare with $\Delta H$?

$$\Delta U = q + w = q - \int_{V_1}^{V_2} P_{ex} \, dV$$

If volume constant: $\Delta U = q_V$ (constant $V$, $V_2 = V_1$)

$q_V$ = heat transferred at constant volume

We saw: $\Delta H = q_p$

Example: Compare $\Delta H$ with $\Delta U$ for
(a) Vaporization of water
(b) Melting of ice

$\Delta H$ & $\Delta U$ similar for condensed phase, but different for gases
Heat capacity: When heat added to material, temperature rises in proportion, \( C \), to the amount of heat added.

\[ q = C \Delta T \]

\( C \) = heat capacity

Heat capacity is extensive property: It depends on the amount of material.

Molar heat capacity:

\[ \bar{C} = C/n = q/(n \Delta T) \quad \text{J K}^{-1} \text{ mol}^{-1} \]

\( n \) = number of moles of substance

\( \bar{C} \) = intensive property

SI units:
Heat capacity:

$C$ depends on how substance is heated.

$q_V = C_V \Delta T \quad C_V = \text{heat capacity at constant volume}$

$q_V = \Delta U \quad \rightarrow \quad C_V = \Delta U / \Delta T$

$q_p = C_p \Delta T \quad C_p = \text{heat capacity at constant pressure}$

$q_p = \Delta H \quad \rightarrow \quad C_p = \Delta H / \Delta T$

$C_p \approx C_v \quad \text{for condensed phases}$

$C_p > C_v \quad \text{for gas phase}$
Thermochemistry: Study of energy changes in chemical reactions.

Heat of reaction: Heat change in transformation from reactants to products at a given temperature and pressure.

Enthalpy change during reaction = heat of reaction

\[ \Delta_r H = q_p \]

\( \Delta_r H < 0 \) (exothermic)

\( \Delta_r H > 0 \) (endothermic)
**Thermochemistry**: Study of energy changes in chemical reactions.

How is heat of reaction measured?

**At constant pressure**, use simple calorimeter:

Only plastic cups & thermometer needed:

Measure $\Delta T$ in medium of known heat capacity: $q_p = C_p \Delta T$

$\Delta_r H = q_p$

**At constant volume**, need “bomb” calorimeter:

Need to keep $V$ fixed: Harder than constant $p$ measurement.
Consider: \[ C(\text{graphite}) + O_2(g) \rightarrow CO_2(g) \]

At \( p = 1 \text{ bar} \left(\approx 1 \text{ atm}\right), \quad T = 298 \text{ K} \):

Heat of conversion of 1 mole \( C(\text{graphite}) \rightarrow 1 \text{ mole } CO_2(g) \)
is measured to be -393.5 kJ, or \( \Delta_r H^\circ = -393.5 \text{ kJ} \).

Denotes standard conditions (1 bar, 298 K)

Usually we define \( \Delta_r H^\circ \) to mean kJ/(mole reaction).

\[ \Delta_r H^\circ = -393.5 \text{ kJ mol}^{-1} \quad \text{for } C + O_2 \rightarrow CO_2 \text{ at 1 bar, 298 K}. \]
For chemical reaction in general:

\[ \Delta_r H^\circ = \sum \nu \Delta_f H^\circ \text{(products)} - \sum \nu \Delta_f H^\circ \text{(reactants)} \]

\[ \Delta_f H^\circ = \text{standard molar enthalpy of formation (kJ mol}^{-1}\text{)} \]

= enthalpy change when 1 mole of compound is formed from constituent elements at \( p = 1 \text{ bar and } T = 298 \text{ K.} \)

\[ \nu = \text{stoichiometric coefficient (no units)} \]

Example: \( CO_2(g) \) formation: \( C\text{(graphite)} + O_2(g) \rightarrow CO_2(g) \)

\[ \Delta_r H^\circ = \Delta_f H^\circ \text{(CO}_2\text{(g)}) - \Delta_f H^\circ \text{(C(graphite))} - \Delta_f H^\circ \text{(O}_2\text{(g))} \]

\[ = -393.5 \text{ kJ mol}^{-1} \text{ (as measured)} \]

Convention: \( \Delta_f H^\circ \text{ of most stable form} = 0. \)
For chemical reaction in general:

Example: $CO_2(g)$ formation: $C$(graphite) + $O_2(g)$ --> $CO_2(g)$

$\Delta_r H^\circ = \Delta_f H^\circ(CO_2(g)) - \Delta_f H^\circ(C$(graphite)) - $\Delta_f H^\circ(O_2(g))$

= -393.5 kJ mol$^{-1}$ (as measured)

Convention: $\Delta_f H^\circ$ of most stable form = 0.

Then: $\Delta_f H^\circ(C$(graphite)) = 0

$\Delta_f H^\circ(O_2(g)) = 0$

Then: $\Delta_r H^\circ = \Delta_f H^\circ(CO_2(g)) = -393.5$ kJ mol$^{-1}$
Thermochemistry: Standard Enthalpy of Formation

\[ \Delta_r H^\circ = \sum \nu \Delta_f H^\circ(\text{products}) - \sum \nu \Delta_f H^\circ(\text{reactants}) \]

How is \( \Delta_f H^\circ \) measured? 2 ways:

**Direct method:** If compound can be directly synthesized from elements, \( \Delta_f H^\circ = \Delta_r H^\circ \), so can be measured as heat of reaction.

Example: \( CO_2(g) \) formation: \( C(\text{graphite}) + O_2(g) \rightarrow CO_2(g) \)

\[ \Delta_f H^\circ(CO_2(g)) = \Delta_r H^\circ = -393.5 \text{ kJ mol}^{-1} \text{ (measured)} \]
Thermochemistry: Standard Enthalpy of Formation

$$\Delta_r H^\circ = \sum \nu \Delta_f H^\circ \text{(products)} - \sum \nu \Delta_f H^\circ \text{(reactants)}$$

How is $\Delta_f H^\circ$ measured? 2 ways:

**Indirect Method:** Much more common. Seldom can compound be made directly from elements. Indirect method is based on Hess’s law.

**Hess’s Law:** When reactants are converted to products, the change in enthalpy is the same whether the reaction takes place in one step or in a series of steps.

Example: $CO \ (g)$ formation: $C(\text{graphite}) + \frac{1}{2}O_2(g) \rightarrow CO \ (g)$

In principle: $\Delta_f H^\circ (CO \ (g)) = \Delta_r H^\circ$ formation; cannot measure $\Delta_r H^\circ (CO \ (g))$. But, reaction competes with $CO_2(g)$ formation; cannot measure $\Delta_r H^\circ (CO \ (g))$. 
Thermochemistry: Standard Enthalpy of Formation

**Hess’s Law:** When reactants are converted to products, the change in enthalpy is the same whether the reaction takes place in one step or in a series of steps.

**Strategy:** Arrange series of chemical equations with known $\Delta_r H^\circ$ that when added up give the same reactants and products of desired reaction.

**Example:**

1. $C(\text{graphite}) + O_2(g) \rightarrow CO_2(g)$  \hspace{1cm} $\Delta_r H^\circ = -393.5 \text{ kJ mol}^{-1}$
2. $CO(g) + (1/2) O_2(g) \rightarrow CO_2(g)$  \hspace{1cm} $\Delta_r H^\circ = -283.0 \text{ kJ mol}^{-1}$

Switch 2. around:

3. $CO_2(g) \rightarrow (1/2) O_2(g) + CO(g)$  \hspace{1cm} $\Delta_r H^\circ = 283.0 \text{ kJ mol}^{-1}$

Add 1. and 3.:

$C(\text{graphite}) + (1/2)O_2(g) \rightarrow CO(g)$  \hspace{1cm} $\Delta_r H^\circ = -110.5 \text{ kJ mol}^{-1}$
Thermochemistry: Standard Enthalpy of Formation

\[ C(\text{graphite}) + \left(\frac{1}{2}\right)O_2(g) \rightarrow CO(g) \quad \Delta_r H^\circ = -110.5 \text{ kJ mol}^{-1} \]

Convention: \( \Delta_f H^\circ \) of most stable form = 0.

Then:
- \( \Delta_f H^\circ (C(\text{graphite})) = 0 \)
- \( \Delta_f H^\circ (O_2(g)) = 0 \)

Then:
- \( \Delta_r H^\circ = \Delta_f H^\circ (CO(g)) = -110.5 \text{ kJ mol}^{-1} \)

Once we know \( \Delta_f H^\circ \) for all reactants and products, we can compute \( \Delta_r H^\circ \) for a particular reaction.

Example: Metabolism breaks down glucose for energy:

\[ C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2 (g) + 6H_2O(\ell) \quad \Delta_r H^\circ = ? \]
Dependence of $\Delta_r H$ on temperature

If we know $\Delta_r H^\circ$ at 298 K, can we calculate $\Delta_r H$ at a different temperature?

Change temperature from $T_1$ to $T_2$

$\Delta_r H_1 = \text{heat of reaction at } T_1$

$\Delta_r H_2 = \text{heat of reaction at } T_2$

at $T_2$: $\Delta_r H_2 = \sum \nu \overline{H}_2 \text{ (products)} - \sum \nu \overline{H}_2 \text{ (reactants)}$

at $T_1$: $\Delta_r H_1 = \sum \nu \overline{H}_1 \text{ (products)} - \sum \nu \overline{H}_1 \text{ (reactants)}$

$$\Delta_r H_2 - \Delta_r H_1 = \Delta \overline{C}_p (T_2 - T_1)$$

$$\Delta \overline{C}_p = \sum \nu \overline{C}_p \text{ (products)} - \sum \nu \overline{C}_p \text{ (reactants)}$$
Example: At T = 298 K, p = 1 bar (≈ 1 atm),

\[ 3O_2(g) \rightarrow 2O_3(g) \quad \Delta_r H^\circ = 285.4 \text{ kJ/mol} \]

What is \( \Delta_r H \) for the reaction at T = 380 K?

\( \overline{C_p}(O_2) = 29.4 \text{ J K}^{-1} \text{ mol}^{-1} \)

\( \overline{C_p}(O_3) = 38.2 \text{ J K}^{-1} \text{ mol}^{-1} \)

Assume \( \overline{C_p} \) is independent of temperature.
Bond enthalpy

Enthalpy of a reaction, $\Delta_r H^\circ$, is related to the enthalpy of the bonds that hold a molecule together.

For example, $H_2(g) \rightarrow 2 \text{ H(g)} \quad \Delta_r H^\circ=436.4 \text{ kJ/mol}$

This is the enthalpy to break the H - H bond.

$\Delta_r H^\circ$ is close to, but not the same as, the energy of the bond.

Recall: $\Delta H = \Delta U + p \Delta V$

$\Delta U = $ energy needed to break bond.

Since $\Delta V > 0$ (1 mole $\rightarrow$ 2 mole), $\Delta H > \Delta U$.

In fact, $\Delta U = 432 \text{ kJ/mol}$ (we’ll discuss how to measure this when we discuss quantum mechanics.)