## The first law of thermodynamics

I. The concept of work, expansion and additional (useful) work.
II. The concept of heat.
III. Definition of internal energy and its molecular interpretation.
IV. Different forms of the first law of thermodynamics.
V. The concept of enthalpy and the necessity of its introduction.
VI. Internal energy of an ideal gas. Joule's experiment.
VII. Internal energy end enthalpy of real gases. The Joule–Thomson effect and the Joule–Thomson coefficient.
VIII. Liquefaction of gases

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## Thermodynamics

- The word 'thermodynamics': Greek origins
  - motion caused by heat + force
- Classification within science:
  - originally only for physical changes (no chemical reactions at all)
  - chemical changes (reaction) : chemical thermodynamics (may be accompanied by physical changes as well)
- Two types:
  - Equilibrium thermodynamics: time is not a factor
  - Irreversible (non-equilibrium) thermodynamics
- Two ways of mathematical handling:
  - Classical thermodynamics
  - Statistical thermodynamics

## The system and its surroundings

- **System**: a part of the 'world', which is of special interest for the examiner, may be surrounded by a 'wall'
- **Surroundings**: the part of the 'world' outside the system

| System type | Matter exchange - type of wall | Energy exchange - type of wall | |
|---|---|---|---|
| Open | Yes - *permeable* - *absence of wall* | Yes - *diathermic* - *moving wall* | (a) Open |
| Closed | No - *impermeable* | Yes - *diathermic* - *moving wall* | (b) Closed |
| Isolated | No - *impermeable* | No - *adiabatic* - *rigid wall* | (c) Isolated |

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## Types of thermodynamic systems

- Based on the spatial distribution of chemical and physical properties:
  - **homogeneous** (the same at every point, e.g. a glass of water)
  - **inhomogeneous** (continuous change, e.g. the atmosphere)
  - **heterogeneous** (discontinuous change, e.g.. coke with ice)
- Based on the direction-dependence of properties:
  - **isotropic** (the same in every direction, e.g. glass)
  - **anisotropic** (differences between directions, e.g. Iceland spar)
- Based on the number of the phases:
  - **monophasic** (e.g. a glass of water)
  - **multiphasic** (water and vapor above it)
- Based on the number of components:
  - **one-component** (e.g. a glass of water, a grain of table salt)
  - **multicomponent** (e.g. sugar solution, salty sugar solution)

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## The properties of the system

- Any property of a thermodynamic systems is either:
  - **extensive**: dependent on the size of the system, i.e. the amount of substance (e.g. mass, volume)
  - **intensive**: independent of the size of the system, i.e. the amount of substance (e.g. temperature, pressure).
  - *if extensive properties are referenced to unit mass (/g, /kg) or amount of substance (/mol), intensive properties are obtained (e.g. density kg/m³, molar volume dm³/mol).*

- Properties can often be measured or calculated on **absolute scales** (e.g. mass; temperature from 0 K).
- Sometimes only possible to measure on a **relative scale** referenced to some arbitrary 0 point (e.g. internal energy; water level in a river).

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## Processes in thermodynamics

- Types of thermodynamic processes (paths) :
  - **spontaneous** *vs.* **forced/non-spontaneous**
  - **reversible** (always through equilibrium states) *vs.* **irreversible** (through non-equilibrium states)
  - **isothermal** (constant temperature, heat exchange with the surroundings is typically necessary) *vs.* **adiabatic** (no heat exchange possible, walls are adiabatic)
  - **isobaric**: at constant pressure (wall moved by pressure changes, e.g. a piston)
  - **isochoric**: at constants volume (the walls of the system are rigid, e.g. autoclave, bomb calorimeter)

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# Energy

Energy is the ability of a system to do work.
- The energy of a system may be changed by <u>work</u>.
  - The energy of the system doing the work decreases.
  - Work done on the system increases the energy.
- Types of work:
  - Mechanical work ($w = Fs$), expansion work, surface expansion, extension, electrical
- The energy of a system may change through <u>heat transfer</u>.
- Between the system and the surroundings
  - heat from surroundings to system (+) or heat from system to surroundings (−): system-centered sign convention!
  - The process in the system may be:
    - **endothermic** = heat absorption (+) or **exothermic** = heat evolution (−)

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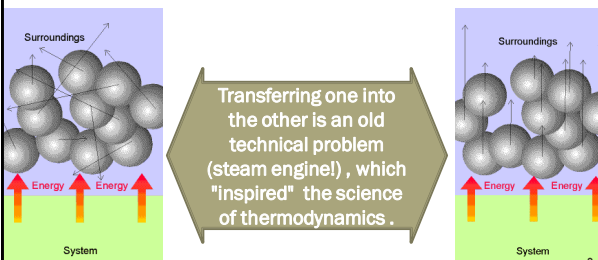# I. The concept of work. Expansion work and additional work.

- Work is always calculated as a product of an intensive and extensive property.

| Type f work | dw | Notations | Units |
|---|---|---|---|
| mechanical | $F\,ds$ | $F$ force<br>$ds$ distance | N<br>m |
| expansion | $-p_{ex}\,dV$ | $p_{ex}$ external pressure<br>$dV$ change in volume | Pa<br>$m^3$ |
| surface expansion | $\gamma\,d\sigma$ | $\gamma$ surface tension<br>$d\sigma$ change in area | N m$^{-1}$<br>$m^2$ |
| extension | $f\,dl$ | $f$ tension<br>$dl$ change in length | N<br>m |
| electrical | $\Phi\,dq$ | $\Phi$ electric potential<br>$dq$ change in charge | V<br>C |

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# II. The concept of heat.

- Molecular interpretation of **heat** $q$ and **work** $w$:
  - **heat**: chaotic motion of molecules (thermal motion)
  - **work**: ordered motion of molecules.

Surroundings

Transferring one into the other is an old technical problem (steam engine!), which "inspired" the science of thermodynamics.

Energy    Energy

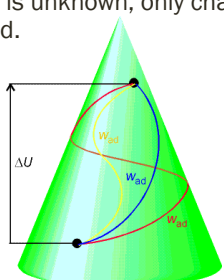System

Surroundings

Energy    Energy

System

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# III. Definition and molecular interpretation of internal energy.

- Thermodynamics requires precise notions of energy:
  - exclude the contributions depending on external forces (kinetic energy of the macroscopic system) or force fields (gravitational, electric)
  - only considers the energy of the system that can be changed by heat and/or work.
- This is the **internal energy** ($U$): the sum of kinetic (rotational, vibrational, translational) an internal (i.e. arising from interaction within the system) potential energies.
- *[Macroscopic kinetic energy or energy caused by external force fields is not included in the internal energy. For example, the heats of combustion or calories for sugar or milk are the same in a moving train, on the top of a mountain or in a deep mine.]*

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# III. Definition and molecular interpretation of internal energy.

- $U$ is extensive and a state function.
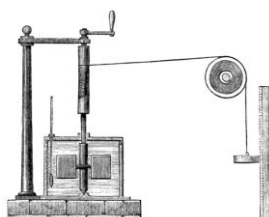- Its absolute value is unknown, only changes can be determined.

$\Delta U$

$w_{ad}$

$w_{ad}$

$w_{ad}$

- Units:
  - 1 N m = 1 joule (J)
  - 1 cal = 4.184 J

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# III. Definition and molecular interpretation of internal energy.

**James Prescott Joule**
(1818-1889)
English physicist

Joule's device for determining the mechanical work equivalent of heat, 1845
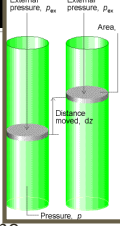
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## IV. The first law of thermodynamics

- The internal energy of a closed system remains constant until work or heat changes it.
  - The change in the internal energy of any system can be calculated from the work and heat:
  - $\Delta U = q + w$   (system-centered sing convention).
- The change in internal energy, $\Delta U$, only depends on the initial and final states:
  - $\Delta U = U_f - U_i$ (= state function)
- Conservation of energy:
  - energy does not form from nothing and cannot be destroyed.
- No *perpetual motion machine* exists.

*Non-deducibility: this is general experience without exceptions!*[13]

## IV. The first law of thermodynamics.
### Work



- Change in *U*:
  - work and/or
  - heat transfer
- **Work**:
  - Work (in general) = force × distance (Nm)
    $dw = -F\,dz$
  - Expansion work = pressure × change in volume (liter×atm)
    $dw = -p_{ex}\,A\,dz = -p_{ex}\,dV$
  - Calculation of work: integration.
  - *[Describing the expansion work of gases is very helpful in developing the exact formalism of thermodynamics.]*

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## IV. The first law of thermodynamics.
### Work

The concept of thermodynamic „**path**" : the conditions under which a process actually occurs.
- The "paths" of isothermal gas expansion *[later adiabatic as well]*:
  - Expansion into vacuum (free expansion):
    $p_{ex} = 0,$   so   $w = 0.$
  - Expansion at constant $p_{ex}$ pressure:
    $p_{ex} =$ **constant**, so the integration is simple:

$$w = -p_{ex}\int_{V_i}^{V_f} dV = -p_{ex}\left(V_f - V_i\right) = -p_{ex}\Delta V$$

  - Both paths are **irreversible**, they do not proceed through equilibrium states.

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## IV. The first law of thermodynamics.
### Work

The concept of thermodynamic „**path**" : the conditions under which a process actually occurs.
- The "paths" of isothermal gas expansion *[later adiabatic as well]*:
  - Expansion against continuously equilibrated pressure,
    - **reversible**: always in equilibrium, an infinitesimal deviation reverses the changes

The value of $p_{ex}$ changes continuously, always equal to the internal pressure p $\Rightarrow$ more complicated integration. Isothermal expansion, pressure $p$ is from the law $pV = nRT$ ($p = nRT/V$) and can be substituted into the formula. The expansion is isothermal, $T =$ const., which simplifies things:

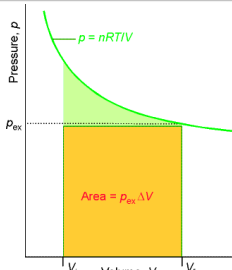$$w = -\int_{V_i}^{V_f} pdV = -\int_{V_i}^{V_f}\frac{nRT}{V}dV = -nRT\int_{V_i}^{V_f}\frac{dV}{V} = -nRT\ln\left(\frac{V_f}{V_i}\right)$$

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## IV. The first law of thermodynamics.
### Work

- Gives the **maximum work** that can be obtained from the system.

- **Indicator diagram**:
  - against vacuum
  - against constant $p_{ex}$ pressure
  - isothermal reversible path

- *[Note: If the volume is constant, no work is done!]*



$$w = -\int_{V_i}^{V_f} pdV = -\int_{V_i}^{V_f}\frac{nRT}{V}dV = -nRT\int_{V_i}^{V_f}\frac{dV}{V} = -nRT\ln\left(\frac{V_f}{V_i}\right)$$

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## IV. The first law of thermodynamics.
### Heat

- **Heat (heat transaction, heat transfer)**:
  - *(for simplicity, exclude any work, expansion, electric, etc.)*
- Heat $q$ (absorption or evolution) at constant volume (isochoric process) is equal to the change in internal energy, $U$, of the system:

  $dU = dq_V$   (where subscript $V$ means constant volume)

- The task is simple and clear: $q$ must be measured at constant $V$.
  - Method: calorimetry.
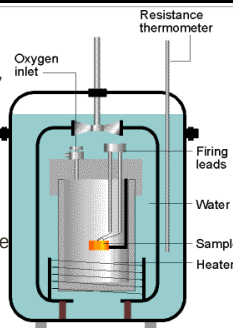  - Device: **bomb calorimeter**.

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## IV. The first law of thermodynamics.
### Heat

- **Bomb calorimeter**:
  - steel vessel with constant volume,
  - adiabatically insulated (no heat exchange with the surroundings),
  - the sample burns in a few second after ignition in a large excess of oxygen.
  - Temperature increase $\Delta T$ is measured, the heat capacity of the calorimeter $C$ is determined separately (using a sample with known heat of combustion):

$$q = C\,\Delta T$$

*(Diagram labels: Resistance thermometer, Oxygen inlet, Firing leads, Water, Sample, Heater)*

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## IV. The first law of thermodynamics.
### Heat

- **Heat capacity** ($C_V$ and $C_p$) is/are very important!
- Heat capacity $C$ measures how the internal energy $U$ changes in response to an increase in temperature.
- Its value depends on the identity of the substance and the experimental conditions:
  - $V$ and
  - $p$.
  - Two cases: either $V$ or $p$ is constant.
    - If $V$ is constant, than heat capacity at constant volume is defined as the partial derivative of U with respect to $T$:

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

  - *[Partial derivative (here): the effect of a single variable on the observed property – with keeping the other variables constant.]*
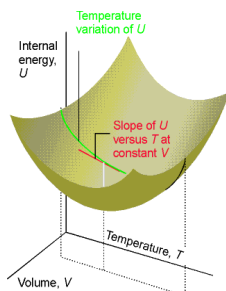
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## IV. The first law of thermodynamics.
### Heat

- Temperature- and volume dependence of $U$: tangent of the $C_p$ versus $T$-, and $C_p$ versus $V$-curves – or surface – at a given point.

- Plots:
  - Only $T$-dependence or
  - $T$- and $V$-dependence.

*(Diagram labels: Temperature variation of $U$, Internal energy, $U$, Slope of $U$ versus $T$ at constant $V$, Temperature, $T$, Volume, $V$)*

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## IV. The first law of thermodynamics.
### Heat

- Different "versions" of heat capacity at constant volume:
  - $C_V$: heat capacity (for a given object); extensive
  - $C_{V,m}$: molar heat capacity (for $n = 1$ mol); intensive
  - $c_V$: specific heat (for 1 kg); intensive

- Direct meaning of heat capacity:
  - Derivative of $U = f(T)$ change: $\quad dU = C_V\,dT$
  - if $C_V$ (in $\Delta T$) is independent of $T$: $\quad \Delta U = C_V\,\Delta T$
  - since $\Delta U = q_V$: $\quad q_V = C_V\,\Delta T$
    This is the basis of the measurement of $C_V$ in a bomb calorimeter.
  - High $C_V$: large heat (removal or input) only causes a small temperature change. *E.g. water, ice.*

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## IV. The first law of thermodynamics.
### Heat

- If $C_V$ heat capacity and $U(T_1)$ is known, the internal energy can be calculated for another $T_2$ temperature:

$$U(T_2) = U(T_1) + \int_{T_1}^{T_2} C_V\,dT$$

- In practice, the change of $U$ during a chemical reaction ($\Delta_r U$) is more important. This can be calculated using the heat capacities of the reactants and products:

$$\Delta_r U(T_2) = \Delta_r U(T_1) + \int_{T_1}^{T_2} \Delta_r c_{V,m}\,dT$$

- Possible complications: temperature dependences of heat capacities:
  $$C_V = a + bT + c/T^2 \text{ (often negligable at small } \Delta T)$$

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## IV. The first law of thermodynamics.
### Heat

- Heat capacity for ideal gases:

  - monatomic gases: as $U_m = U_m(0) + 3/2\,RT$, so
    $C_{V,m} = (\partial U_m / \partial T)_V = 3/2\,R = [12{,}47 \text{ J K}^{-1}\text{mol}^{-1}]$

  - diatomic gases:
    $C_{V,m} = 5/2\,R = [20{,}785 \text{ J K}^{-1}\text{mol}^{-1}]$

  - nonlinear multiatomic gases:
    $C_{V,m} = 3R = [24{,}94 \text{ J K}^{-1}\text{mol}^{-1}]$

  - *Heat capacity values are important because they are <u>accurate</u> and thus are used widely in calculating the various thermodynamic quantities.*

- https://www.youtube.com/watch?v=0xhtszEjNN0

## V. Enthalpy.

Enthalpy, *H:* state function for the description of processes at constant pressure v.
- ΔH: heat transfer at constant pressure assuming no additional work.
- *Definition: H = U + pV*
- (In addition to *U*, it also contains the expansion work necessarily accompanying the chemical reaction.)
- state function: $\Delta H = H_f - H_i$
- extensive (molar enthalpy $H_m$ is intensive!)
- no absolute value known, arbitrary scale.

- *[Important: ΔH also means heat at constant **pressure**, whereas ΔU means heat at constant **volume**.]*

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## V. Enthalpy.

Determining <u>changes</u> in enthalpy:
- in l, s phase, *ΔV* is typically small, so $H_m \approx U_m$.
- in gas phase: flame calorimeter (gas+$O_2$)
  - spiral tube at constant pressure,
  - adiabatic (insulated),
  - continuous gas + $O_2$ inflow,
  - continuous burning,
  - continuous product outflow.

Gas, vapour
Oxygen
Products
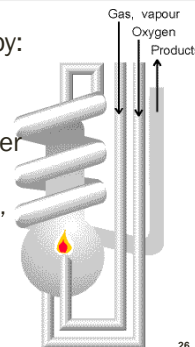
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## V. Enthalpy.

- Temperature dependence of enthalpy: slope of the function *H = f(T) = heat capacity at constant pressure; $C_p$.*
- "Versions" of $C_p$ – similarly to $C_V$:
  - $C_p$: heat capacity (for a given object) – *extensive*
  - $C_{p,m}$: *molar heat capacity* (for *n* = 1 mol) – *intensive*
  - $c_p$: *specific heat* (for 1 kg) – *intensive*
- Direct meaning of $C_p$ – similarly to $C_V$:
  - Derivative of *H = f(T)* change:     *dH = $C_p$ dT*
  - if $C_p$ (in *ΔT*) is independent of *T*:    *ΔH = $C_p$ ΔT*
  - since *ΔH = $q_p$*:             *$q_p$ = $C_p$ ΔT*
- temperature dependence of $C_p$:
  $C_p = a + bT + c/T^2$ (often negligable at small *ΔT*)

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## V. Enthalpy.

- From the $C_p$ heat capacity, the *H* enthalpy of a given system can be calculated for different temperatures:

$$H(T_2) = H(T_1) + \int_{T_1}^{T_2} C_p dT$$

- In practice, the temperature-dependence of the enthalpy of a (chemical) reaction is more important. This can be calculated from the appropriate weighted sum of the heat capacities of the substances participating in the reactions:

$$\Delta_r H(T_2) = \Delta_r H(T_1) + \int_{T_1}^{T_2} \Delta_r C_{p,m} dT$$

- In thermochemistry, this is called **Kirchhoff's law**.

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## V. Enthalpy.
### Connection between the two heat capacities

- When heated, gases extend, and through the *volume work* involved, they transmit some of the warming heat to the environment. Consequently, the constant pressure heat capacity ($C_p$) is higher than the constant volume heat capacity ($C_V$).

- In **real gases**, intermolecular forces must be overcome.

| Work | ideal gas | real gas |
|------|-----------|----------|
| On the atmosphere | yes | yes |
| On internal bonds | no | yes |

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## V. Enthalpy.
### Connection between the two heat capacities

- **For an ideal gas** (only important for gases anyway):
  - *difference of the two heat capacities: $C_p - C_V = nR$,*
    for 1 mol of gas: $C_{p,m} - C_{V,m} = R$
  - *ratio: $C_{p,m}/C_{V,m} = \gamma$ [**heat capacity ratio**].*
  - Reversible adiabatic expansion of an ideal gas:
    $pV^\gamma = constant$

| Work | ideal gas | real gas |
|------|-----------|----------|
| On the atmosphere | yes | yes |
| On internal bonds | no | yes |

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## VI. Internal energy of the ideal gas.
### Joule's experiment.

- The internal energy ($U$) and enthalpy ($H$) of a system depend on the temperature ($T$). This dependence is expressed on the heat capacities, $C_p$ and $C_V$.
- The question arises: do these values depend on other – $p$, $V$ – properties? How does the internal energy ($U$) change if we change $T$ or $V$ or $p$?
- Look at the effects of 2 properties out of the 3 as the third one is "constrained„ (see: gas law). For example, the effect of changing:
  - $V$ and
  - $T$.
- *[We can show how thermodynamics can be constructed with the methods of mathematics.]*

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## VI. Internal energy of the ideal gas.
### Joule's experiment.

- If $V \to V + dV$ (at constant $T$), then $U \to U$ ', in a general notation:

$$U' = U + \left(\frac{\partial U}{\partial V}\right)_T dV$$

- If $T$ increases to $T + dT$ (at constant $V$), then *[similarly]*:

$$U' = U + \left(\frac{\partial U}{\partial T}\right)_V dT$$

- Assume that the change in $V$ and $T$ is infinitesimal:

$$U' = U + \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$

- Exact differential:

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$

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## VI. Internal energy of the ideal gas.
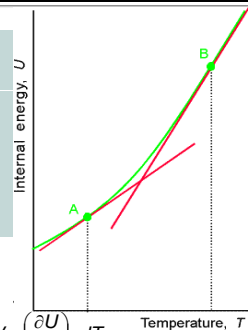### Joule's experiment.

- Exact differential means:
  - The change in $U$ depends on the change in $V$ and $T$, the individual variables are the partial derivatives.
  - This can be depicted in a 3D coordinate system:

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$

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## VI. Internal energy of the ideal gas.
### Joule's experiment.

- Exact differential in a 3D coordinate system:
- The effect of one or the other is the intersection of the surface with a plane, which is in a 2D coordinate system:

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$

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## VI. Internal energy of the ideal gas.
### Joule's experiment.

The two partial derivatives have physical meaning:
- $(\partial U/\partial V)_T = \pi_T$, a **internal pressure** (change in $U$ with $V$).
- $(\partial U/\partial T)_V = C_V$, a **molar heat capacity at constant volume**.

Equation for $dU$:

$$dU = \pi_T dV + C_V dT$$

- $C_V$ is always positive.
- $\pi_T$ is expected to be different for ideal and real gases. In the latter, the attractive and repulsive forces between particles result in some internal pressure, whereas it is zero for an ideal gas.

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## VI. Internal energy of the ideal gas.
### Joule's experiment.

- **Joule's experiment**: how does $U$ depend on the volume?
- <u>Isotherm</u> expansion of gas against vacuum: Joule *did not experience any change in temperature*.
- Conclusion: $U$ does not depend on volume, so $(\partial U/\partial V)_T = \pi_T = 0$ (true for an ideal gas).
- The experience was imprecise, but the errors were small so the conclusion was correct.
- Later, the Joule-Thomson experiment gave accurate results.

Thermometer

High pressure gas    Vacuum
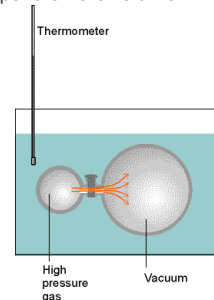
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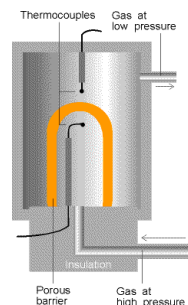## VII. Internal energy and enthalpy of real gases. The Joule-Thomson effect

- **Adiabatic changes**: so far, heat exchange between the system and the environment was allowed, not now.
- The work of the **adiabatic gas expansion** (now not against the vacuum): the real gas cannot absorb heat from its environment when extending, so, it *cools down*. Consequently, the adiabatic extent is *not isothermal*!
- *[This also follows from the molecular approach:*
  - *during expansion, the forces of attraction between the gas molecules must be overcome, which is covered by the internal energy, U,*
  - *the pV product depends on the pressure, and $p_1V_1 \neq p_2V_2$, it also varies. The ratio of these two sets the value of μ (Joule-Thomson coefficient).]*

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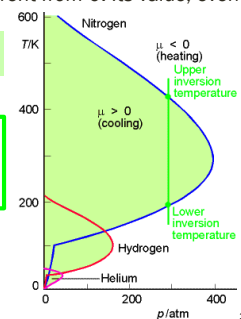## VII. Internal energy and enthalpy of real gases. The Joule-Thomson effect

- Expansion of a gas through a barrier (porous wall): cools down during expansion (conditions are **insulated**, i.e. **adiabatic**). This is called the **Joule–Thomson effect**.
- Characterization: adiabatic **Joule–Thomson coefficient** ($\mu$):
$$\mu = (\partial T/\partial p)_H$$
- it measures the temperature change in response to a pressure change. *This has major practical importance.*



## VII. Internal energy and enthalpy of real gases. The Joule-Thomson effect

- For real gases, $\mu$ is typically different from 0. Its value, even its sign depends on $T$:
  - *if $\mu > 0$*, the gas cools down upon expansion,
  - if $\mu < 0$, the gas heats up upon expansion.
  - Below the inversion temperature $T_i$, $\mu < 0$ always holds,
  - but there is another $T_i$ where $\mu$ changes sign again.



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## VII. Internal energy and enthalpy of real gases. The Joule-Thomson effect

- The Joule–Thomson effect and **compression cooling**:

1. The gas is compressed by electric energy, its temperature increases.
2. In rear or outer cooling coils, the gas cools down to room temperature (here, the gas "heats the room up").
3. Room-temperature compressed gas is led into the inner part and is expanded through a porous barrier: it cools down and also cools the inner chamber.
4. The cold gas is led back to the compressor and the cycle begins again.
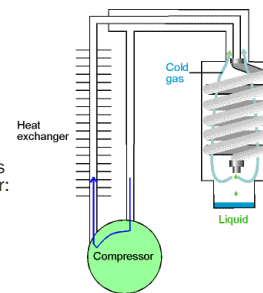


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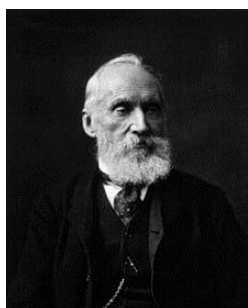


**William Thomson
(1824-1907)
Irish mathematician, physicist**
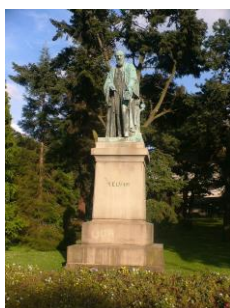
**statue of Lord Kelvin
Belfast, botanical garden**

41

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