Physical Chemistry lecture

Part 2.2 First law of thermodynamics

2.2.1. The Joule experiment and its consequences
2.2.2. Heat, heat capacity - meaning and calculation
2.2.3. Work - sense and calculation
2.2.4. Internal energy and enthalpy
2.2.5. Consequences of the first law of thermodynamics
2.2.6. Calculation of changes in internal energy and enthalpy

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| 2.2. 2 | **Internal Energy (intrinsic)** |

$$E_u = E_k + E_p + U$$

The **total energy** of a particle is the sum of its kinetic and potential energies

$$E = E_k + E_p \qquad \text{(F.8)}$$

The total energy of a thermodynamic system is equal to the sum of the macroscopic kinetic energy, the macroscopic potential energy and the remainder called the internal energy

In general, it is sufficient to know the energy **increments** (changes) during thermodynamic transformations rather than the total energy of the system. The reference state for which the internal energy of a body is taken to be zero can be taken arbitrarily.
In calculations involving physical thermodynamic transformations, it is not necessary to take into account those components of internal energy that do not change during the process under consideration, e.g. nuclear energy and chemical energy.

The internal energy of a system includes:
- kinetic energy of the progressive and rotational motion of the particles
- energy of oscillatory motion of atoms in the particle
- potential energy in the mutual attraction field of the particles
- energy of electron states
- chemical energy, associated with the possibility of rearrangement of the particles
- nuclear energy

A body may possess two kinds of energy, kinetic energy and potential energy. The **kinetic energy**, E_k, of a body is the energy the body possesses as a result of its motion. For a body of mass m travelling at a speed v

$$E_k = \tfrac{1}{2}mv^2 \qquad \boxed{\text{Kinetic energy}} \qquad (F.4)$$

The **potential energy**, E_p or more commonly V, of a body is the energy it possesses as a result of its position. No universal expression for the potential energy can be given because it depends on the type of force that the body experiences. For a particle of mass m at an altitude h close to the surface of the Earth, the gravitational potential energy is

$$V(h) = V(0) + mgh \qquad \boxed{\begin{array}{c}\text{Gravitational}\\ \text{potential energy}\end{array}} \qquad (F.5)$$

where g is the **acceleration of free fall** ($g = 9.81$ m s^{-2}). The zero of potential energy is arbitrary, and in this case it is common to set $V(0) = 0$.

One of the most important forms of potential energy in chemistry is the **Coulomb potential energy**, the potential energy of the electrostatic interaction between two point electric charges. For a point charge Q_1 at a distance r in a vacuum from another point charge Q_2

$$V(r) = \frac{Q_1 Q_2}{4\pi\varepsilon_0 r} \qquad \boxed{\begin{array}{c}\text{Coulomb}\\ \text{potential energy}\end{array}} \qquad (F.6)$$

interaction between two charges is reduced, and the vacuum permittivity is replaced by the **permittivity**, ε, of the medium. The permittivity is commonly expressed as a multiple of the vacuum permittivity

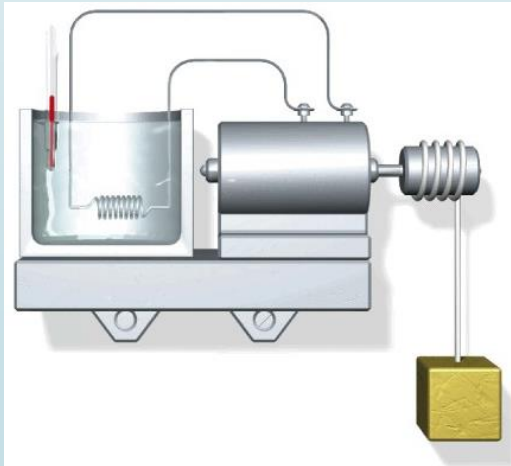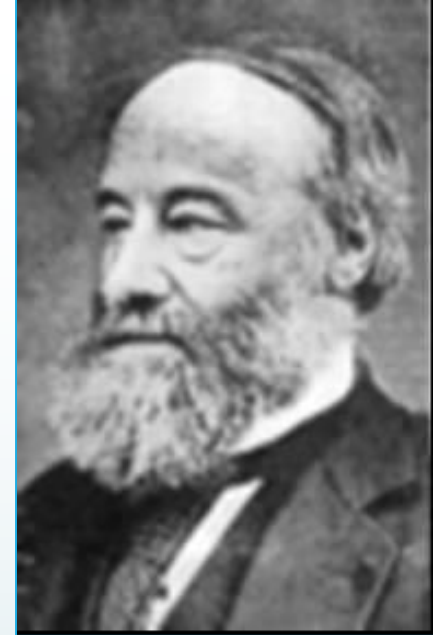$$\varepsilon = \varepsilon_r \varepsilon_0 \qquad (F.7)$$

with ε_r the dimensionless **relative permittivity** (formerly, the *dielectric constant*).

2.2. 4   **Principle of conservation of energy**

$$\Delta U = Q + W$$

$$dU = Q_{el} + W_{el}$$

Heat and work

2.2. 5

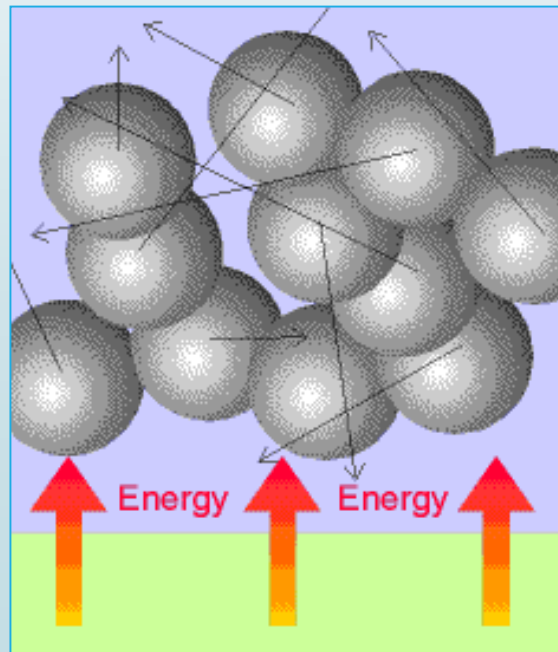Heat and work are modes of transfer, not types of energy.
If the sole cause of the flow of a certain amount of energy between a system and its surroundings is a temperature difference, then this energy is called energy transferred in the manner of heat, or heat for short . If the total effect of the flow of a certain amount of energy between the system and the surroundings can be reduced to the vertical displacement of some weight, this amount of energy is called energy transferred in the manner of mechanical work, or mechanical work for short .
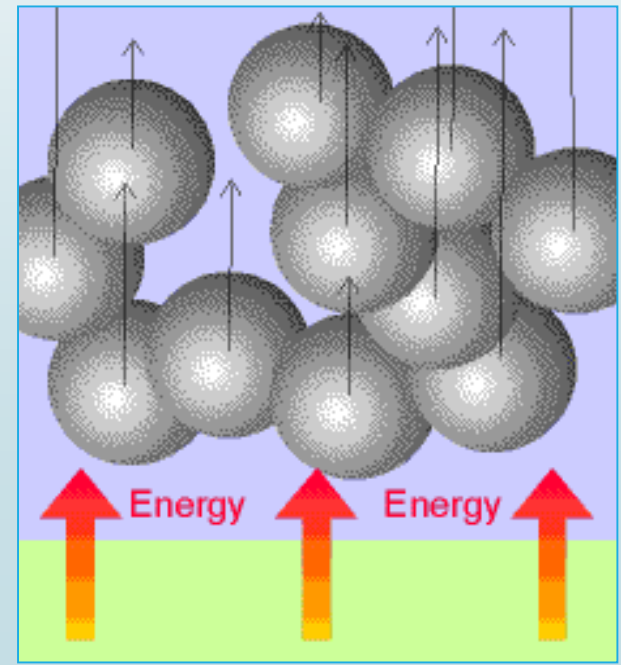
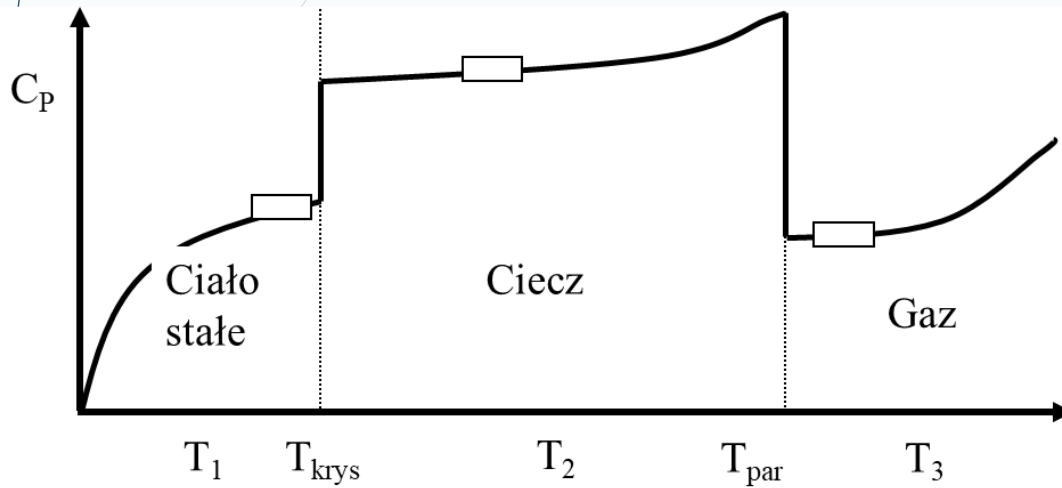**Molecular interpretation of heat and work**

Heat exchange   Work exchange

Environment

Energy   Energy   Energy   Energy

System

2.2. 6 **Heat capacity**

$$Q = C \cdot m \cdot \Delta T$$

$$\frac{dQ(T)}{dT} = C(T)$$

C_P

Ciało stałe

Ciecz

Gaz

T_1 T_{krys} T_2 T_{par} T_3

$$Q = m \int_{T_1}^{T_2} C(T)dT$$

the amount of heat exchanged when the temperature of a unit quantity of the system changes by one degree

$$C_P, C_V \left[\frac{J}{mol \cdot K}\right] \qquad c_P, c_V \left[\frac{J}{g \cdot K}\right]$$

$$C_P = M \cdot c_P \qquad C_V = M \cdot c_V$$

Example 2.4 *Evaluating an increase in enthalpy with temperature*

$$\int_{H(T_1)}^{H(T_2)} \mathrm{d}H = \int_{T_1}^{T_2} \left(a + bT + \frac{c}{T^2} \right) \mathrm{d}T$$

$$\int \mathrm{d}x = x + \text{constant} \qquad \int x\,\mathrm{d}x = \tfrac{1}{2}x^2 + \text{constant} \qquad \int \frac{\mathrm{d}x}{x^2} = -\frac{1}{x} + \text{constant}$$
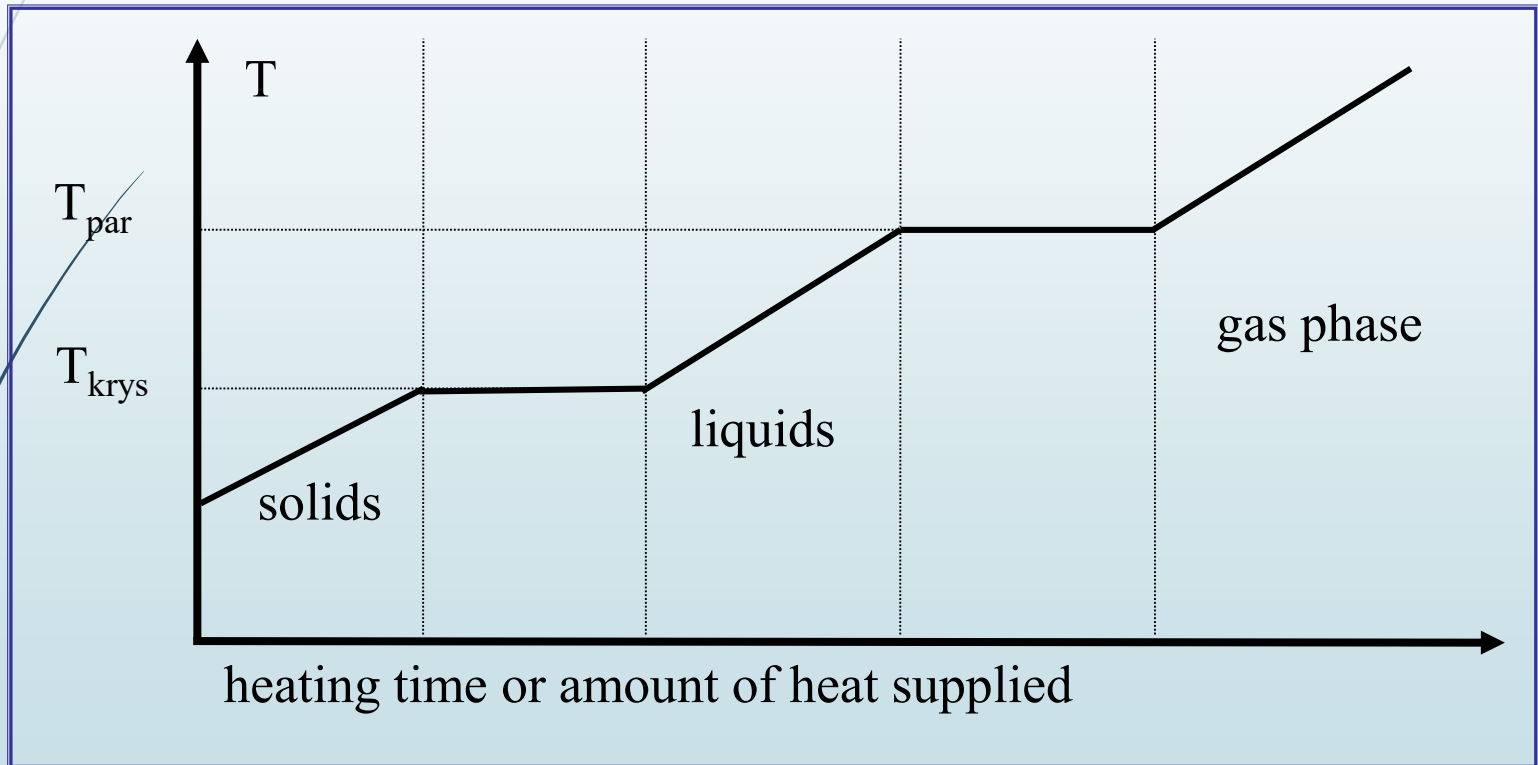
$$H(T_2) - H(T_1) = a(T_2 - T_1) + \tfrac{1}{2}b(T_2^2 - T_1^2) - c\left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

2.2. 8

Transformation heat

melting
crystallisation
evaporation
condensation
Sublimation
resublimation

$$Q = L \cdot m$$

T

T_{par}

T_{krys}

solids

liquids

gas phase

heating time or amount of heat supplied
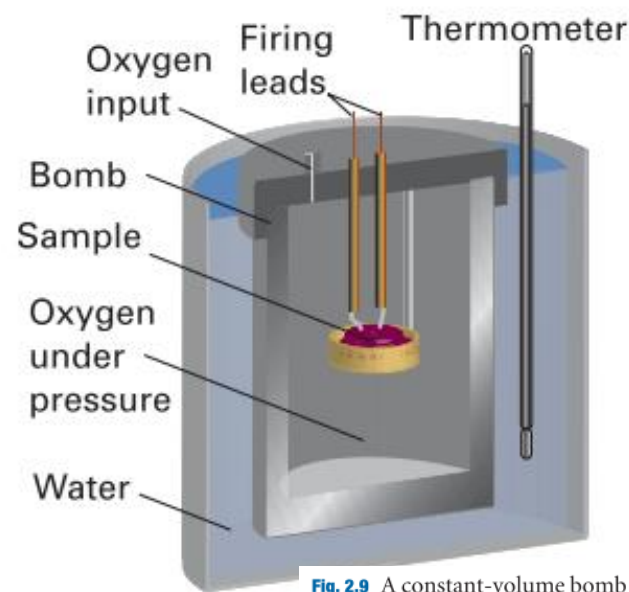
(a) Calorimetry

Calorimetry is the study of heat transfer during physical and chemical processes. A **calorimeter** is a device for measuring energy transferred as heat. The most common device for measuring ΔU is an **adiabatic bomb calorimeter** (Fig. 2.9). The process we wish to study—which may be a chemical reaction—is initiated inside a constant-volume container, the 'bomb'. The bomb is immersed in a stirred water bath, and the whole device is the calorimeter. The calorimeter is also immersed in an outer water bath. The water in the calorimeter and of the outer bath are both monitored and adjusted to the same temperature. This arrangement ensures that there is no net loss of heat from the calorimeter to the surroundings (the bath) and hence that the calorimeter is adiabatic.

Fig. 2.9 A constant-volume bomb calorimeter. The 'bomb' is the central vessel, which is strong enough to withstand high pressures. The calorimeter (for which the heat capacity must be known) is the entire assembly shown here. To ensure adiabaticity, the calorimeter is immersed in a water bath with a temperature continuously readjusted to that of the calorimeter at each stage of the combustion.

• A brief illustration

If we pass a current of 10.0 A from a 12 V supply for 300 s, then from eqn 2.14 the energy supplied as heat is

$$q = (10.0 \text{ A}) \times (12 \text{ V}) \times (300 \text{ s}) = 3.6 \times 10^4 \text{ A V s} = 36 \text{ kJ}$$
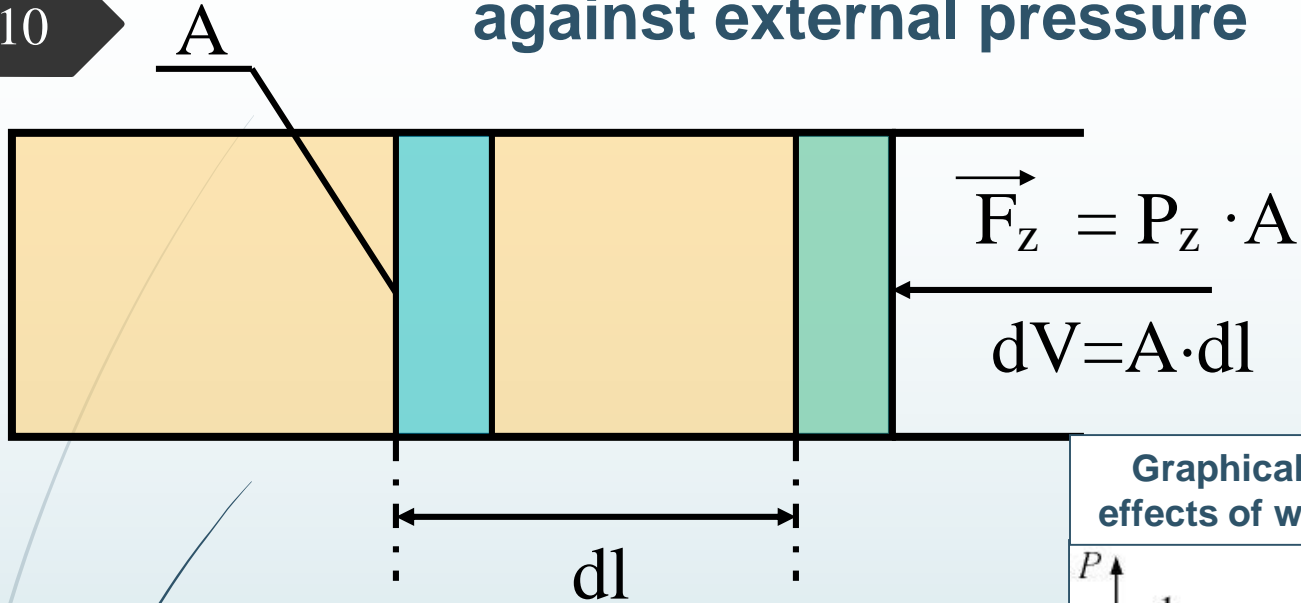
because 1 A V s = 1 J. If the observed rise in temperature is 5.5 K, then the calorimeter constant is $C = (36 \text{ kJ})/(5.5 \text{ K}) = 6.5 \text{ kJ K}^{-1}$. •

Volumetric expansion work against external pressure

2.2. 10

A

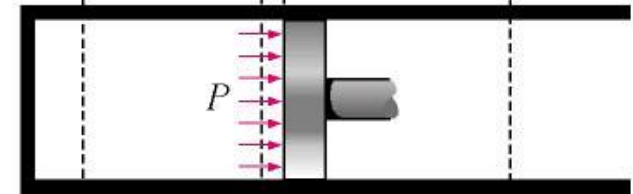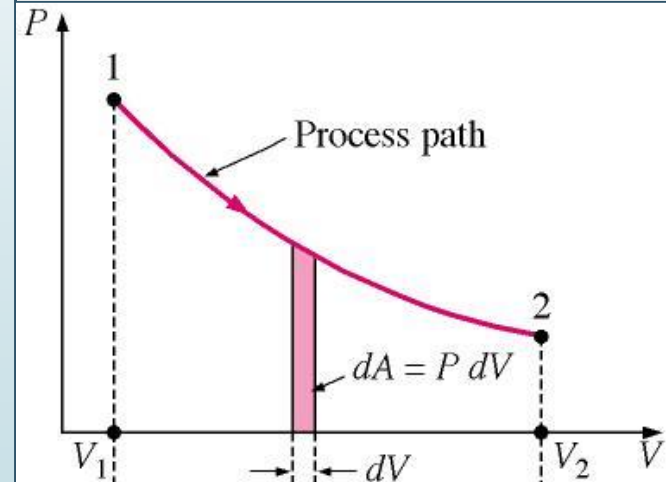$$\overrightarrow{F_z} = P_z \cdot A$$

$$dV = A \cdot dl$$

dl

$$W_{el,vol} = -\vec{F}_z dl = -P_z dV$$

$$W_{volumetric} = -\int_{path} P_z dV$$

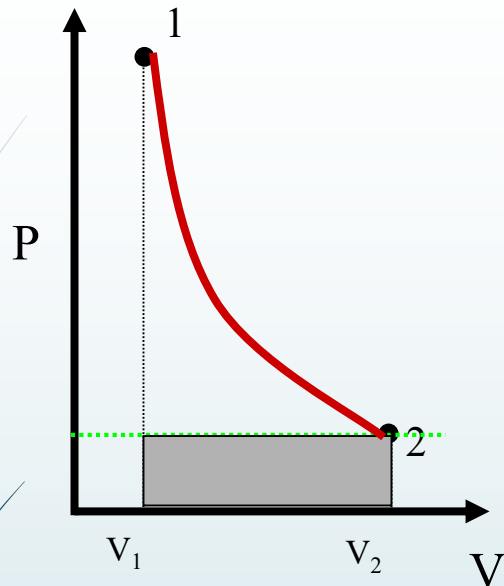trzeba znać funkcję p(V,T)

Graphical interpretation of the effects of working under pressure

Reversible and irreversible process work

P

1

V₁ .... V₂

V_1 V_2

V

P

1

isotherm

2

V

Isobaric expansion

$$W_{el} = -P_{zew}dV$$

in the case of expansion to vacuum
P=0 => W=0

$$\Delta U = Q$$
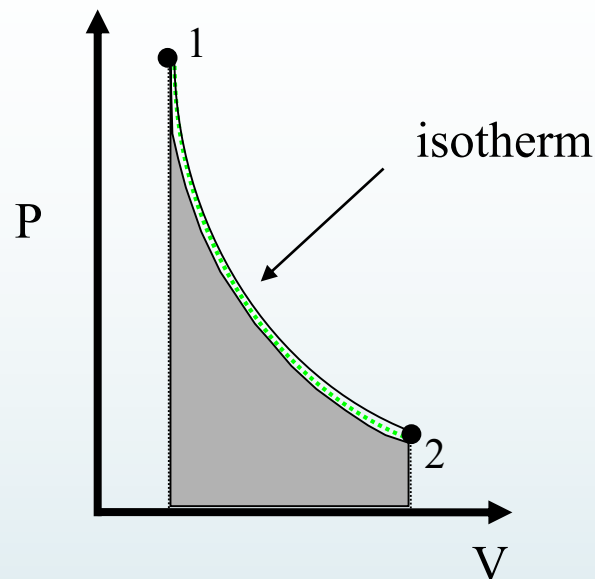
Isothermal expansion

$$W = -\int_{V_1}^{V_2} PdV = -\int_{V_1}^{V_2} \frac{nRT}{V}dV$$

$$P = \frac{nRT}{V}$$

$$W = -nRT(\ln(V_2) - \ln(V_1)) = -nRT\ln\left(\frac{V_2}{V_1}\right)$$

Special case: isochoric process
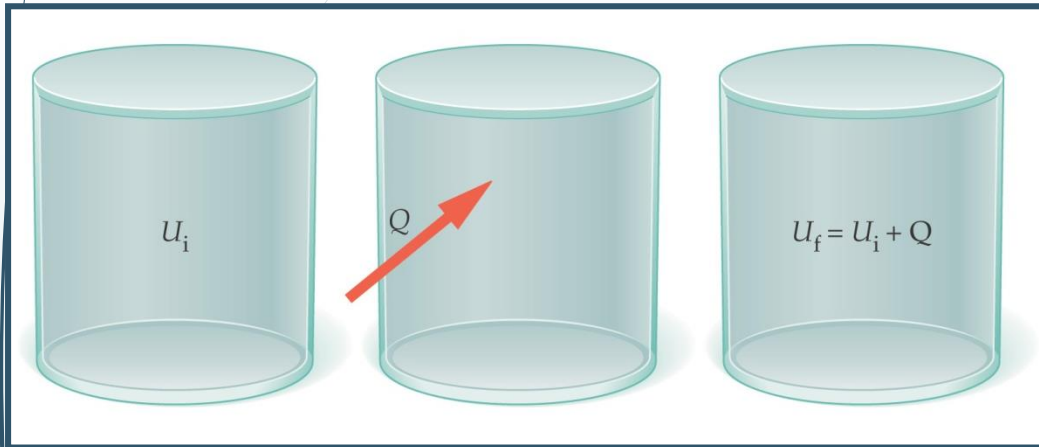
$$W = -p\Delta V = 0$$

$$dU_V = Q_{el,V}$$

$$\Delta U_V = Q_V$$

$$W_b = \int_1^2 PdV = 0$$

$$\Delta U = Q = n\, C_V\, \Delta T$$

Types of work

2.2. 13

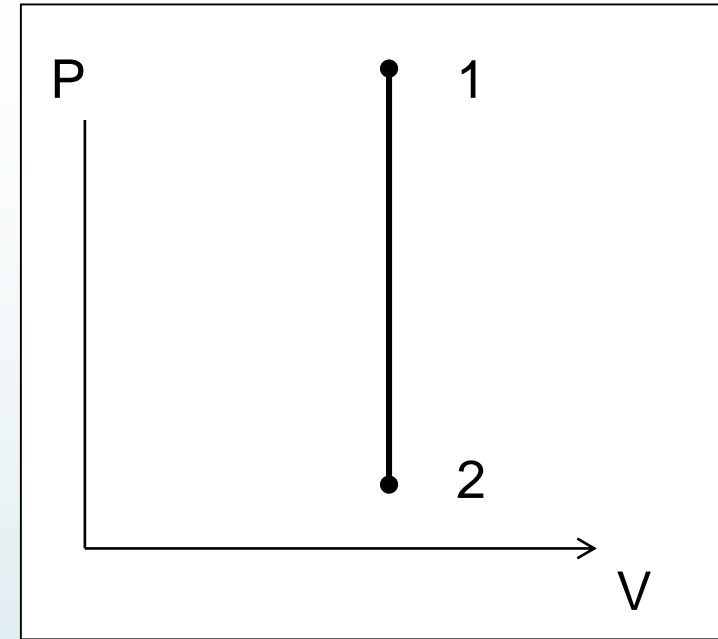| Work	Force generalised	Path generalised	Elementary work
expansion	pressure (P)	volume (V)	$-PdV$
electrical	electrtric force (E)	charge (Q)	$-EdQ$
surface	surface tension (σ)	surface area (A)	$-\sigma dA$

Internal energy is a function of state

$$dU = Q_{el} + W_{el}$$
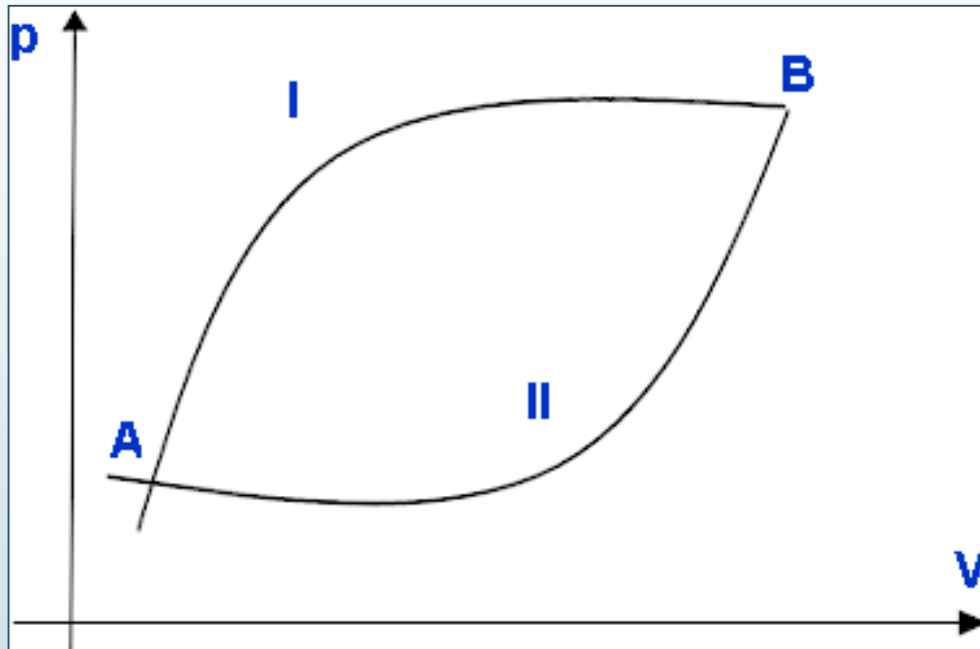
The amount of work done depends on the path - it is not a function of the state

The amount of heat exchanged depends on the path - it is not a function of state

$$U = U(T, V, \xi)$$

$$dU = \left(\frac{\partial U}{\partial T} \right)_{V,\xi} dT + \left(\frac{\partial U}{\partial V} \right)_{T,\xi} dV + \left(\frac{\partial U}{\partial \xi} \right)_{T,V} d\xi$$

$$\left(\frac{\partial U}{\partial T} \right)_{V,\xi} = C_v \qquad \left(\frac{\partial U}{\partial \xi} \right)_{T,V} = Q_{r,V}$$

$$\left(\frac{\partial U}{\partial V} \right)_{T,\xi} = -p + T \left(\frac{\partial p}{\partial T} \right)_{V,\xi}$$

Consequences of the first principle of thermodynamics

2.2. 16

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

$$\left(\frac{\partial U}{\partial T}\right)_p = \pi_T \left(\frac{\partial V}{\partial T}\right)_p + C_V$$

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{p,\xi}$$

	$\alpha/(10^{-4}\,\mathrm{K}^{-1})$
Liquids	
Benzene	12.4
Carbon tetrachloride	12.4
Ethanol	11.2
Mercury	1.82
Water	2.1
Solids	
Copper	0.501
Diamond	0.030
Iron	0.354
Lead	0.861

The values refer to 20 °C
Data: AIP(α), KL(κ_T).

Expansion coefficient
Its large values imply large volume changes with temperature change under isobaric conditions and in the absence of chemical reactions

Consequences of the first principle of thermodynamics

2.2. 17

Example

Calculation of the coefficient of expansion for a perfect gas

$$\alpha_T = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{1}{V}\left(\frac{\partial (nRT/p)}{\partial T}\right)_p = \frac{nR}{pV} = \frac{1}{T}$$

The higher the temperature, the smaller the effect on the volume change

What about unit and plot?

2.2. 18 — Enthalpy

- **Enthalpy is a function of state.**
- **What is the point of introducing a new thermodynamic quantity?**

•- When carrying out a thermodynamic transformation under isochoric conditions, heat transfer is unambiguously correlated with a change in internal energy and temperature.

•- Solids and liquids do not change their volume in a significant number of transformations. Isochoric conditions are, therefore, provided by the nature of these systems. Even carrying out transformations on them under isobaric conditions, isochoricity is also fulfilled.

•- Gases no longer have this characteristic, and under isobaric conditions a process of compression or expansion takes place during heat transfer and temperature change. This means that work is done on the surroundings or on the system.

•-Theinternal energy changesthen do not correspond to the measured heat effect - it is reduced by the amount of work done. In other words, by supplying heat, the temperature does not rise as much as it does in an isochoric transformation.

•Under isobaric conditions, it is the change in enthalpy that is the measure of the heat exchanged.

2.2. 19

Enthalpy

$$H \overset{df}{=} U + pV = H(T, p, \xi)$$

$$dH = \left(\frac{\partial H}{\partial T}\right)_{p,\xi} dT + \left(\frac{\partial H}{\partial p}\right)_{T,\xi} dp + \left(\frac{\partial H}{\partial \xi}\right)_{T,p} d\xi$$

$$\left(\frac{\partial H}{\partial T}\right)_{p,\xi} = C_P \qquad\qquad \left(\frac{\partial H}{\partial \xi}\right)_{T,p} = Q_{r,p}$$

$$\left(\frac{\partial H}{\partial p}\right)_{T,\xi} = V - T\left(\frac{\partial V}{\partial T}\right)_{p,\xi}$$

2.2. 20

The first law of thermodynamics formulated based on the enthalpy

$$H = U + pV$$

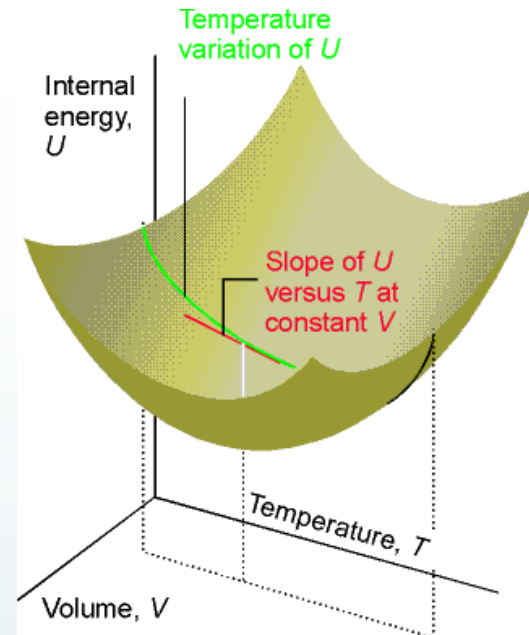$$dH = dU + d(pV) = dU + pdV + Vdp$$

$$dU = Q_{el} - pdV$$

$$dH = Q_{el} - pdV + pdV + Vdp$$

$$\boxed{dH = Q_{el} + Vdp}$$

Consequences of the first principle of thermodynamics

2.2. 21

Temperature variation of U

Internal energy, U

Slope of U versus T at constant V

Temperature, T

Volume, V

$$C_V = \lim_{\Delta T \to 0} \frac{Q_V}{\Delta T} \implies C_V = \left(\frac{\partial U}{\partial T} \right)_V$$

$$Q(T_A \to T_B)_V = U_B - U_A = n \int_{T_A}^{T_B} \left(\frac{\partial U}{\partial T} \right)_V dT = n \int_{T_A}^{T_B} C_{V,m} dT$$

$$C_P = \lim_{\Delta T \to 0} \frac{Q_P}{\Delta T} \implies C_P = \left(\frac{\partial H}{\partial T} \right)_P$$

$$Q(T_A \to T_B)_P = H_B - H_A = n \int_{T_A}^{T_B} \left(\frac{\partial H}{\partial T} \right)_P dT = n \int_{T_A}^{T_B} C_{P,m} dT$$

Consequences of the first principle of thermodynamics

2.2. 22 **Temperature dependence of enthalpy**

in the absence of progress of the chemical reaction:

$$dH = C_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp$$

It can be proven (see thermodynamic identities) that:

$$\left(\frac{\partial H}{\partial T}\right)_V = \left(1 - \frac{\alpha \cdot \mu}{\kappa_T}\right) \cdot C_p$$

isothermal compressibility coefficient

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T,\xi}$$

Joule-Thomson coefficient

$$\mu = \left(\frac{\partial T}{\partial p}\right)_{H,\xi}$$

Conclusion:
Since this equation is valid for any substance and all quantities are measurable, the temperature dependence of enthalpy can be known at any temperature.

Consequences of the first principle of thermodynamics

| 2.2. 23 | **Isothermal compressibility coefficient** |

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T,\xi}$$

Example values of the compressibility coefficient

This coefficient always has a positive value. The minus sign compensates for the fact that the volume decreases due to the increase in pressure.

	$\kappa_T/(10^{-6}\,\text{atm}^{-1})$
Liquids	
Benzene	92.1
Carbon tetrachloride	90.5
Ethanol	76.8
Mercury	38.7
Water	49.6
Solids	
Copper	0.735
Diamond	0.187
Iron	0.589
Lead	2.21

💡 **Example**

Calculation of the isothermal compressibility coefficient for an ideal gas

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T,\xi} = -\frac{1}{V}\left(\frac{\partial(nRT/p)}{\partial p}\right)_T = \frac{-nRT}{V}\left(-\frac{1}{p^2}\right) = \frac{1}{p}$$

Joule-Thomson Effect

2.2. 24

Device for measuring the Joule-Thomson effect. A gas expands through a porous thermally insulated barrier. This corresponds to isoenthalpic expansion:

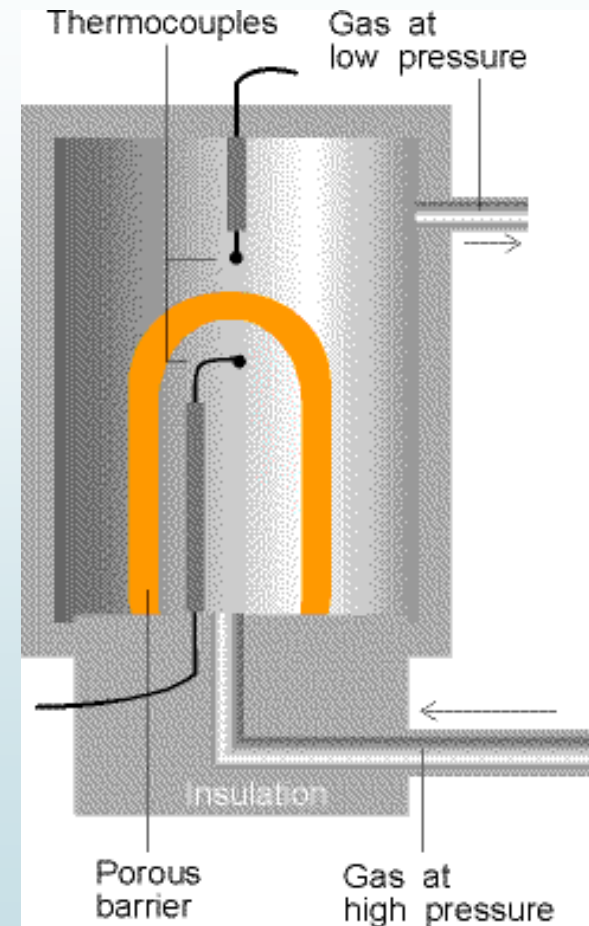### Change in internal energy of flowing gas:

$$U_k - U_p = w = p_p V_p - p_k V_k$$

$$U_k + p_k V_k = U_p + p_p V_p$$

$$\boxed{H_k = H_p}$$

On the lower pressure side, a lower temperature is observed, and the temperature difference is proportional to the pressure difference. The change in temperature due to pressure change, i.e. the Joule'-Thomson coefficient, is measured.

$$\mu = \left(\frac{\partial T}{\partial p} \right)_{H,\xi}$$

Thermocouples   Gas at low pressure

Insulation

Porous barrier   Gas at high pressure

Joule-Thomson Effect

2.2. 25

It is more convenient to measure the Joule-Thomson coefficient by the indirect method using the isothermal Joule-Thomson coefficient
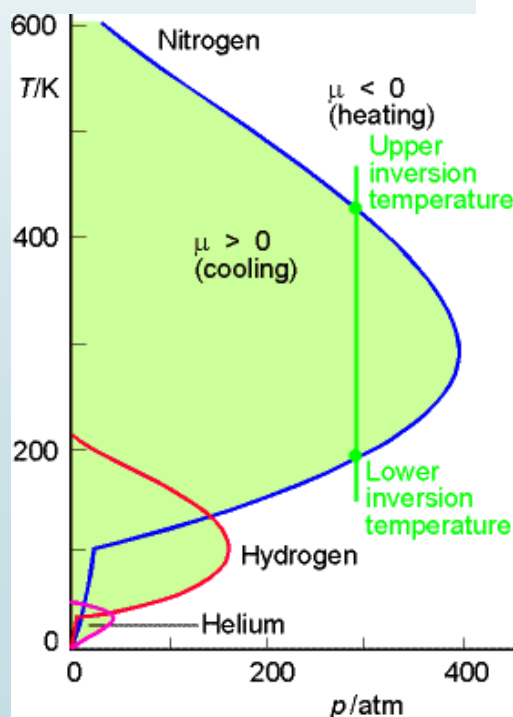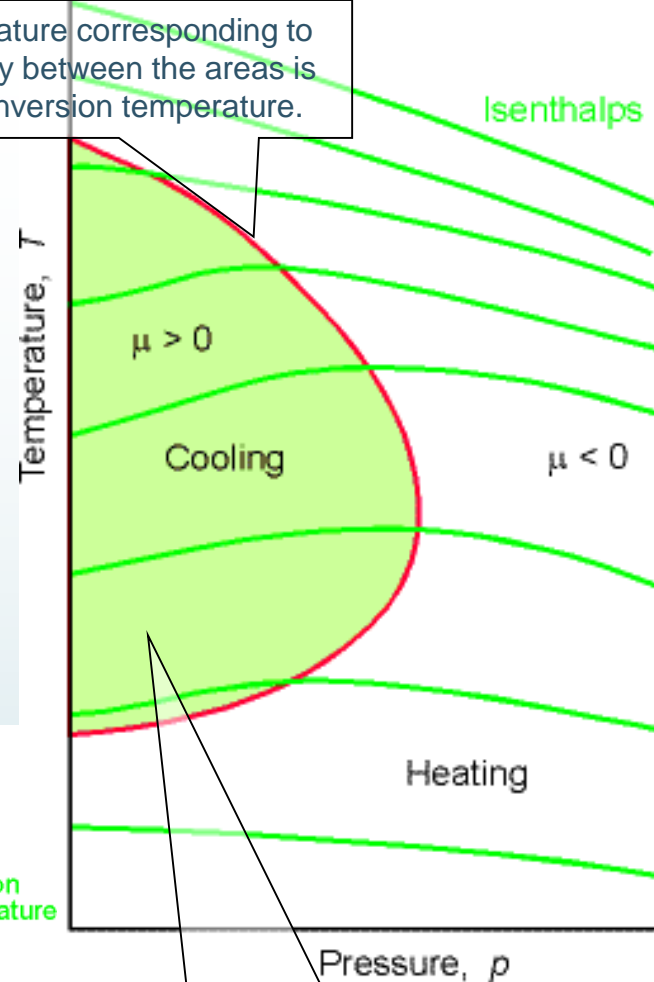
$$\mu = \left(\frac{\partial T}{\partial p}\right)_{H,\xi} \qquad \mu_T = \left(\frac{\partial H}{\partial p}\right)_{T,\xi}$$

The relationship between both coefficients

$$\mu_T = -C_p\mu$$

Znak współczynnika μ zależy od warunków termodynamicznych.

The temperature corresponding to the boundary between the areas is called the inversion temperature.
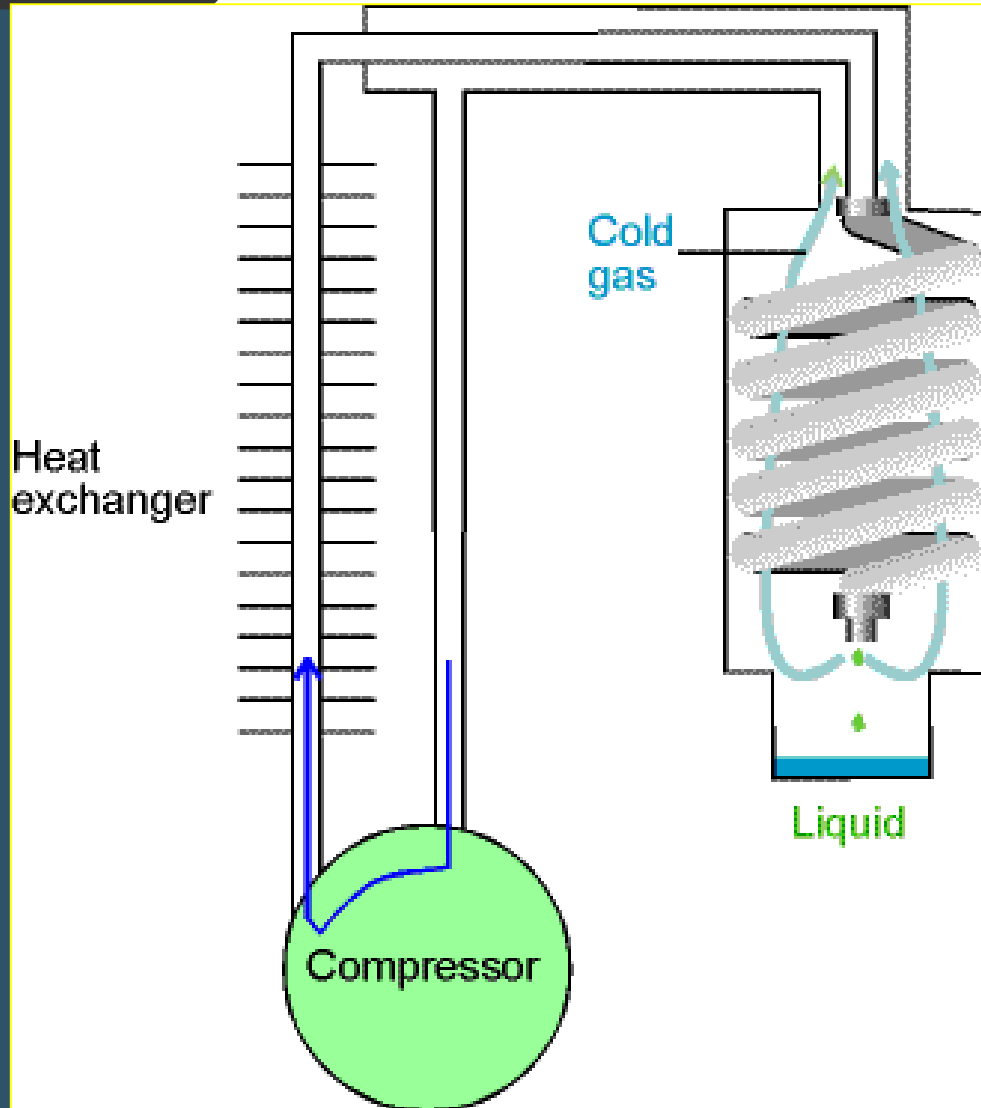
Isenthalps

To achieve a cooling effect, the temperature must be below the inversion temperature. Adiabatic pressure reduction causes movement along isoenthalpic curves.There is an upper and a lower inversion temperature

Joule-Thomson Effect

Principle of operation of the Linde refrigerator

Cold gas

Heat exchanger

Liquid

Compressor

The circulating gas below the inversion temperature, flowing through the partition between the tanks of different pressures, is cooled during expansion. The cooled gas pre-cools the gas at higher pressure, which is further cooled as it expands. Finally, the gas condenses and flows to the bottom of the vessel.

Relationship between ΔH° and ΔU° ...

How different is internal energy from enthalpy?

$$\Delta H^o = H^o_{prod} - H^o_{substr} = \sum_{prod} v'_i H^o_i - \sum_{substr} v_i H^o_i$$

$$\Delta H^o = \sum_{prod} v'_i \left(U^o_i + P^o V_i \right) - \sum_{substr} v_i \left(U^o_i + P^o V \right) =$$

$$\sum_{prod} v'_i U^o_i - \sum_{substr} v_i U^o_i + P^o \Delta V = \Delta U^o + P^o \Delta V$$

since V$_{gaz}$ >> V$_{condensed}$

$$\Delta V = \sum_{prod} v'_i V_i - \sum_{substr} v_i V_i$$

$$\Delta V = \sum_{\substack{prod \\ gazowe}} v'_i V_i - \sum_{\substack{substr \\ gazowe}} v_i V_i = \Delta v_g \frac{RT}{P^o}$$

$$\boxed{\Delta H^o = \Delta U^o + \Delta v_g RT}$$

💡 **Example**

2.2. 28

$$Al_2O_{3(corundum)} + 3SO_{2(g)} = Al_2(SO_4)_{3(s)}$$

at T=298K and under pressure of 1 atm, 579 kJ was released. Calculate the heat of this reaction at constant volume.

$$Q_V = Q_p + \Delta n(RT)$$

Δn=0-3=-3

$$Q_V = -579000 + (-3) \cdot 8.314 \cdot 298 = -586\,kJ$$

Example 2.2 *Relating ΔH and ΔU*

The change in molar internal energy when $CaCO_3(s)$ as calcite converts to another form, aragonite, is $+0.21$ kJ mol^{-1}. Calculate the difference between the molar enthalpy and internal energy changes when the pressure is 1.0 bar given that the densities of the polymorphs are 2.71 g cm^{-3} and 2.93 g cm^{-3}, respectively.

Method The starting point for the calculation is the relation between the enthalpy of a substance and its internal energy (eqn 2.18). The difference between the two quantities can be expressed in terms of the pressure and the difference of their molar volumes, and the latter can be calculated from their molar masses, M, and their mass densities, ρ, by using $\rho = M/V_m$.

Answer The change in enthalpy when the transition occurs is

$$\Delta H_m = H_m(\text{aragonite}) - H_m(\text{calcite})$$
$$= \{U_m(a) + pV_m(a)\} - \{U_m(c) + pV_m(c)\}$$
$$= \Delta U_m + p\{V_m(a) - V_m(c)\}$$

$$\Delta H_m - \Delta U_m = pM\left(\frac{1}{\rho(a)} - \frac{1}{\rho(c)}\right)$$

where a denotes aragonite and c calcite. It follows by substituting $V_m = M/\rho$ that

Substitution of the data, using $M = 100$ g mol^{-1}, gives

$$\Delta H_m - \Delta U_m = (1.0 \times 10^5 \text{ Pa}) \times (100 \text{ g mol}^{-1}) \times \left(\frac{1}{2.93 \text{ g cm}^{-3}} - \frac{1}{2.71 \text{ g cm}^{-3}}\right)$$

$$= -2.8 \times 10^5 \text{ Pa cm}^3 \text{ mol}^{-1} = -0.28 \text{ Pa m}^3 \text{ mol}^{-1}$$

Hence (because 1 Pa m^3 = 1 J), $\Delta H_m - \Delta U_m = -0.28$ J mol^{-1}, which is only 0.1 per cent of the value of ΔU_m. We see that it is usually justifiable to ignore the difference between the molar enthalpy and internal energy of condensed phases, except at very high pressures, when $p\Delta V_m$ is no longer negligible.

Self-test 2.2 Calculate the difference between ΔH and ΔU when 1.0 mol Sn(s, grey) of density 5.75 g cm^{-3} changes to Sn(s, white) of density 7.31 g cm^{-3} at 10.0 bar. At 298 K, $\Delta H = +2.1$ kJ. $\qquad\qquad [\Delta H - \Delta U = -4.4\ J]$

The enthalpy of a perfect gas is related to its internal energy by using $pV = nRT$ in the definition of H:
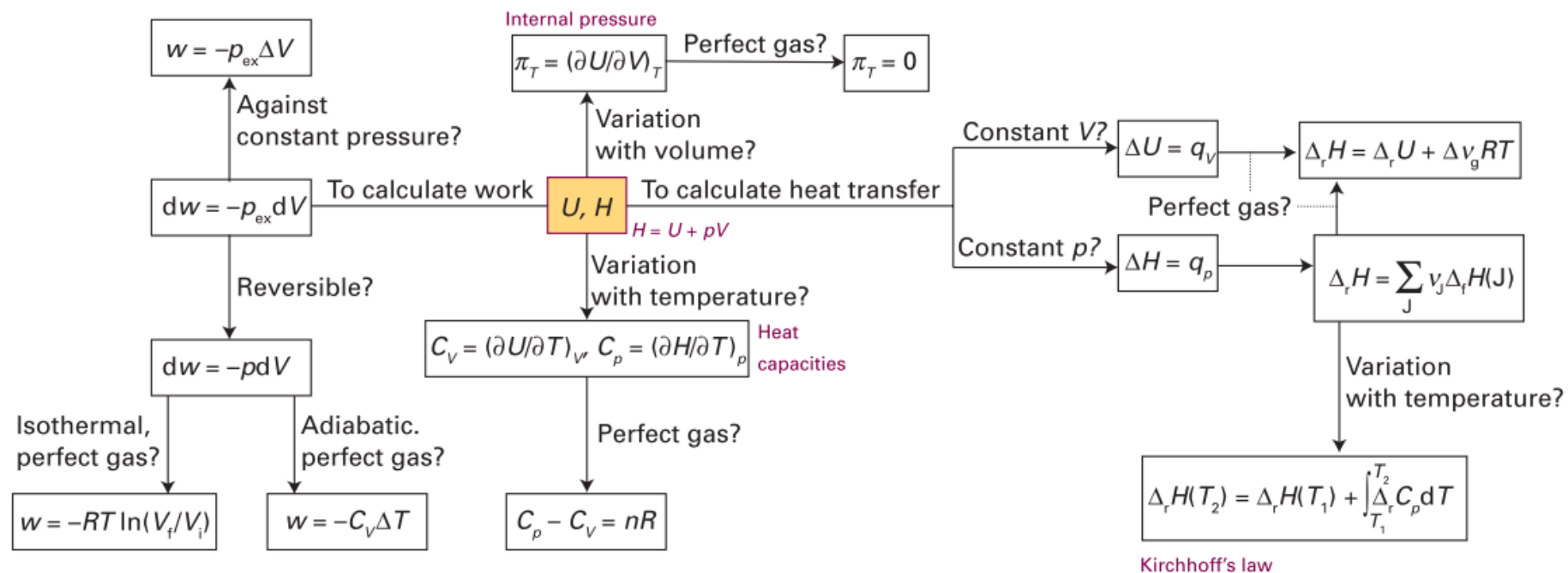
$$H = U + pV = U + nRT \qquad\qquad (2.20)°$$

This relation implies that the change of enthalpy in a reaction that produces or consumes gas is

$$\Delta H = \Delta U + \Delta n_{g} RT \qquad\qquad (2.21)°$$

where Δn_{g} is the change in the amount of gas molecules in the reaction.

The First Law (Chapter 2)

Internal pressure

$$w = -p_{ex}\Delta V$$

$$\pi_T = (\partial U/\partial V)_T$$

Perfect gas?

$$\pi_T = 0$$

Against constant pressure?

Variation with volume?

Constant V?

$$\Delta U = q_V$$

$$\Delta_r H = \Delta_r U + \Delta v_g RT$$

$$dw = -p_{ex}dV$$

To calculate work

$$U, H$$

To calculate heat transfer

Perfect gas?

$$H = U + pV$$

Constant p?

$$\Delta H = q_p$$

$$\Delta_r H = \sum_J v_J \Delta_f H(J)$$

Reversible?

Variation with temperature?

$$dw = -pdV$$

$$C_V = (\partial U/\partial T)_V, \quad C_p = (\partial H/\partial T)_p$$

Heat capacities

Variation with temperature?

Isothermal, perfect gas?

Adiabatic. perfect gas?

Perfect gas?

$$w = -RT\ln(V_f/V_i)$$

$$w = -C_V\Delta T$$

$$C_p - C_V = nR$$

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

Kirchhoff's law

2 The First Law

The basic concepts

2.1 Work, heat, and energy

2.2 The internal energy

2.3 Expansion work

2.4 Heat transactions

2.5 Enthalpy

I2.1 Impact on biochemistry and materials science: Differential scanning calorimetry

2.6 Adiabatic changes

Self study: what is DSC?

IMPACT ON BIOCHEMISTRY AND MATERIALS SCIENCE
I2.1 Differential scanning calorimetry