University of Science
Department of Materials science

CHAPTER 2
THE FIRST LAW OF THERMODYNAMICS

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Nhiệt động lực học cho Vật liệu - LVH-PVV

Outline

1. Introduction
2. The Relationship between Heat and Work
3. Internal Energy and the First Law of Thermodynamics
4. Constant-Volume Processes
5. Constant-Pressure Processes and the Enthalpy *H*
6. Heat Capacity
7. Reversible Adiabatic Processes
8. Reversible Isothermal Pressure or Volume Changes of an Ideal Gas

Types of Processes

Isothermal Processes:

- A process in which Temperature of the system remains constant though other variables may change.
- Transformations at constant temperature ($dT = 0$)

Isochoric Processes:

- A process in which volume of the system remains constant though other variables may change.
- Transformations at constant volume ($dV = 0$ or $d\alpha = 0$)

Isobaric Processes:

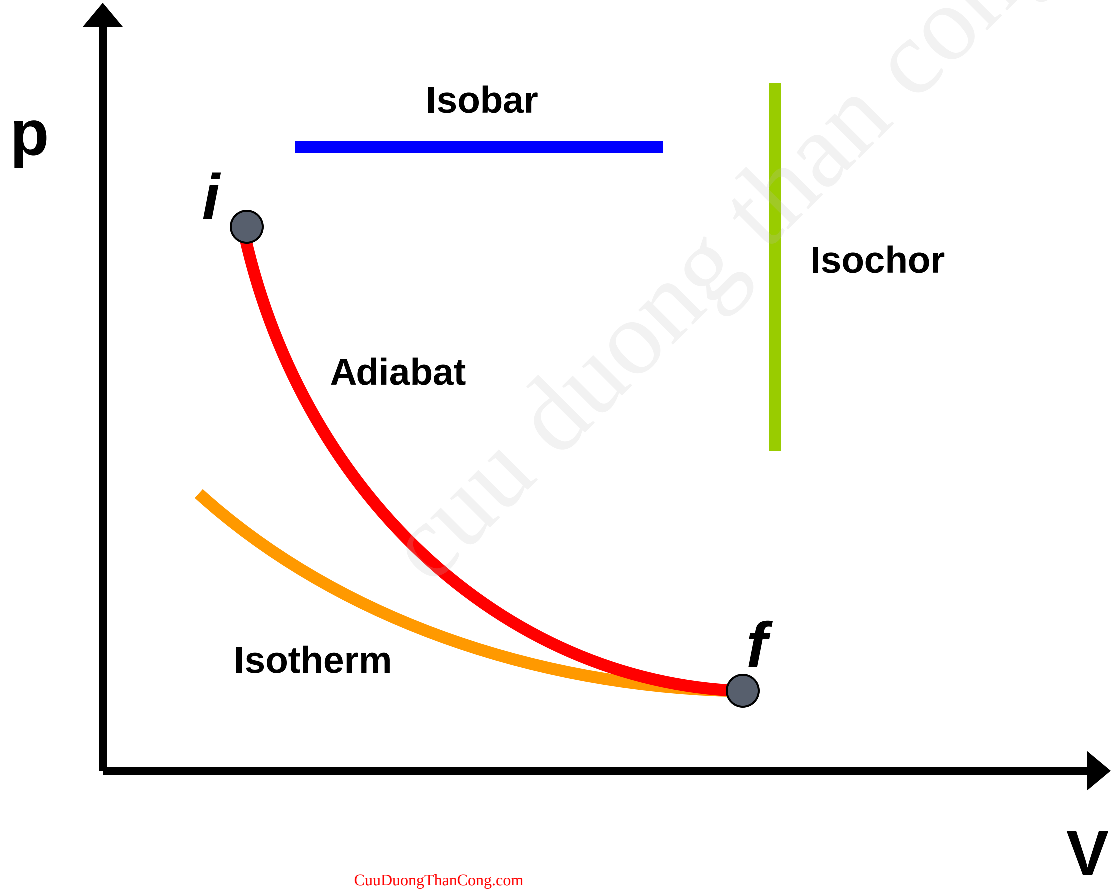
- A process in which pressure of the system remains constant though other variables may change
- Transformations at constant pressure ($dp = 0$)

Adiabatic processes:

- A process in which no heat is exchanged is with the surroundings.
- Transformations **without** the exchange of heat between the environment and the system ($dQ = 0$ or $dq = 0$)

Adiabatic Processes

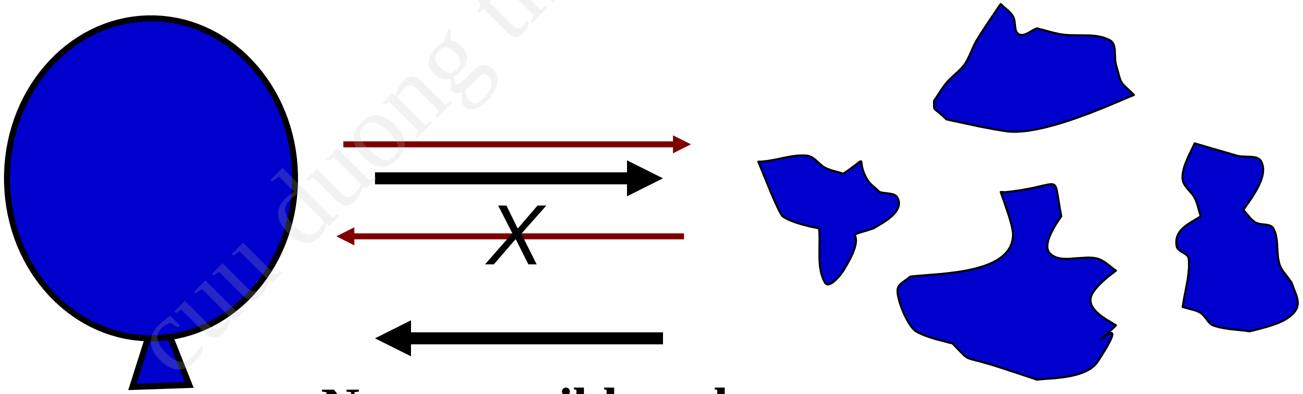
P-V Diagrams:



2.1 INTRODUCTION

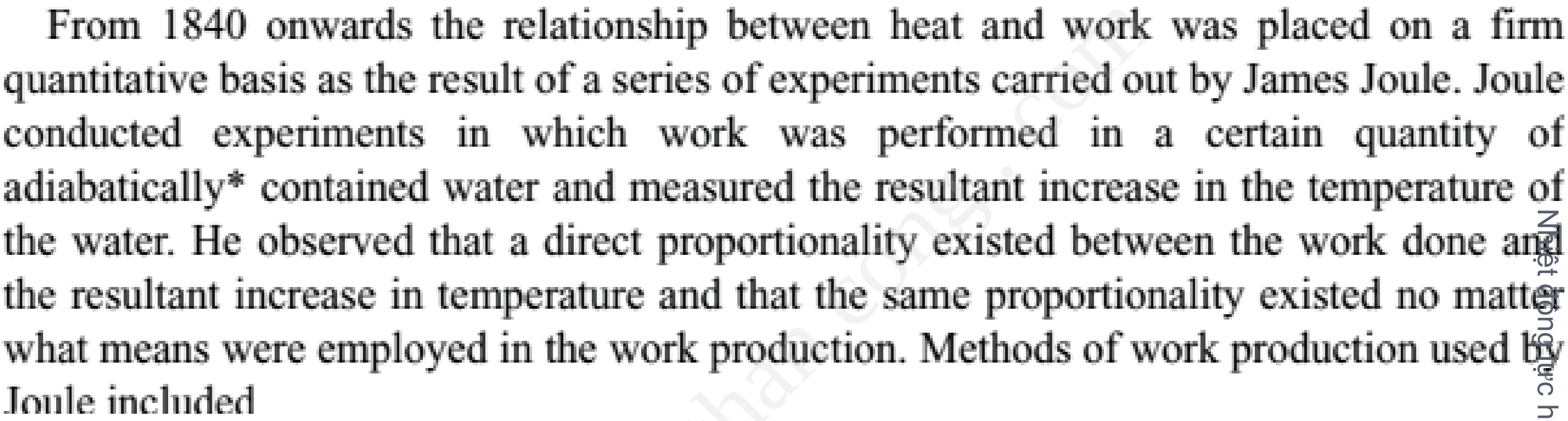
EXAMPLE: POPPING A BALLOON

- A “reversible process” can go in either direction, but these processes are rare.
- Generally, the irreversibility shows up as waste heat

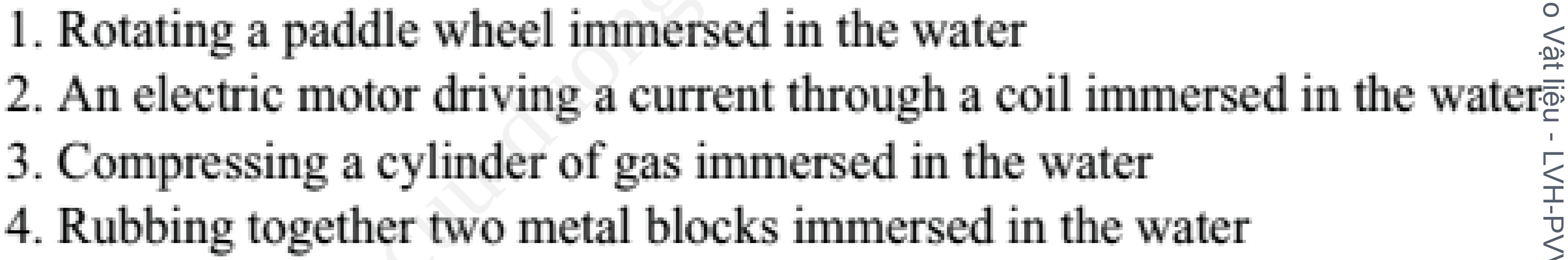


Not reversible unless energy is expended

2.2 THE RELATIONSHIP BETWEEN HEAT AND WORK



From 1840 onwards the relationship between heat and work was placed on a firm quantitative basis as the result of a series of experiments carried out by James Joule. Joule conducted experiments in which work was performed in a certain quantity of adiabatically* contained water and measured the resultant increase in the temperature of the water. He observed that a direct proportionality existed between the work done and the resultant increase in temperature and that the same proportionality existed no matter what means were employed in the work production. Methods of work production used by Joule included



1. Rotating a paddle wheel immersed in the water
2. An electric motor driving a current through a coil immersed in the water
3. Compressing a cylinder of gas immersed in the water
4. Rubbing together two metal blocks immersed in the water

Heat

... is the amount of internal energy entering or leaving a system

... occurs by conduction, convection, or radiation.

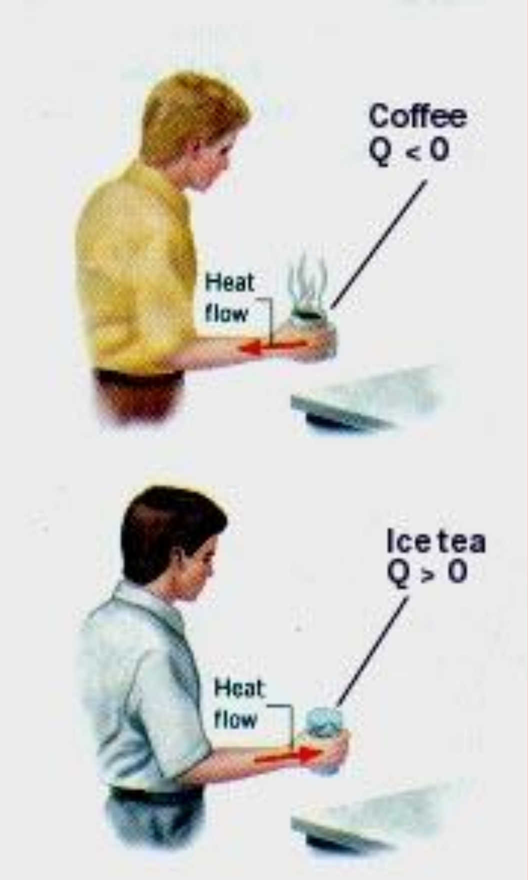
... causes a substance's temperature to change

... is not the same as the internal energy of a substance

... is positive if thermal energy flows *into* the substance

... is negative if thermal energy flows *out of* the substance

... is measured in joules



2.3 INTERNAL ENERGY AND THE FIRST LAW OF THERMODYNAMICS

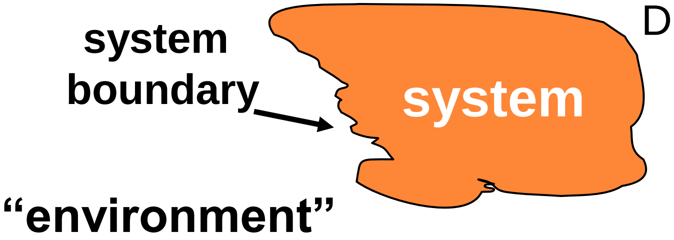
First Law of Thermodynamics

energy can neither be created nor destroyed

2.3 INTERNAL ENERGY AND THE FIRST LAW OF THERMODYNAMICS

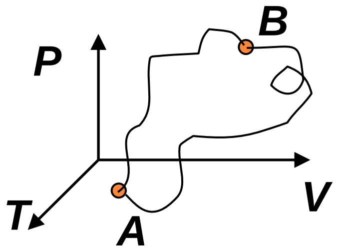
INTERNAL ENERGY

The ***internal energy*** of a system of particles, ***U***, is the sum of the kinetic energy *in the reference frame in which the center of mass is at rest* and the potential energy arising from the forces of the particles on each other.



Difference between the total energy and the internal energy?

U = kinetic + potential



The internal energy is a **state function** – it depends only on the values of macroparameters (the state of a system), not on the method of preparation of this state (the "path" in the macroparameter space is irrelevant).

In equilibrium [f (P,V,T)=0] : $\boldsymbol{U = U(V, T)}$

U depends on the kinetic energy of particles in a system and an average inter-particle distance (~ $\boldsymbol{V^{-1/3}}$) – interactions.

For an ideal gas (no interactions) : $\boldsymbol{U = U(T)}$ **- "pure" kinetic**

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Internal Energy (U or E)

: (measured in joules)

- Sum of random translational, rotational, and vibrational kinetic energies

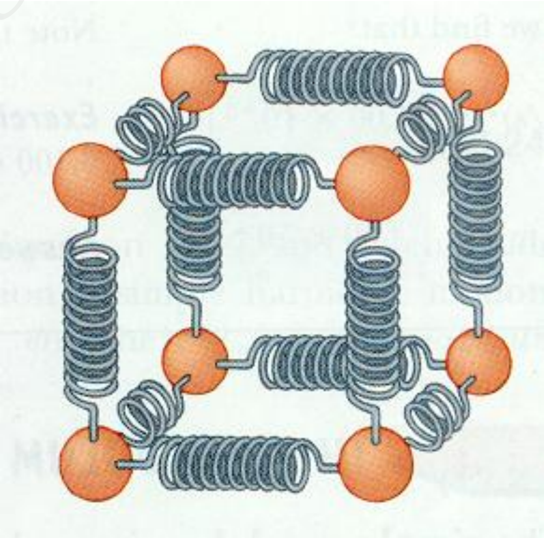
ΔU: change in U

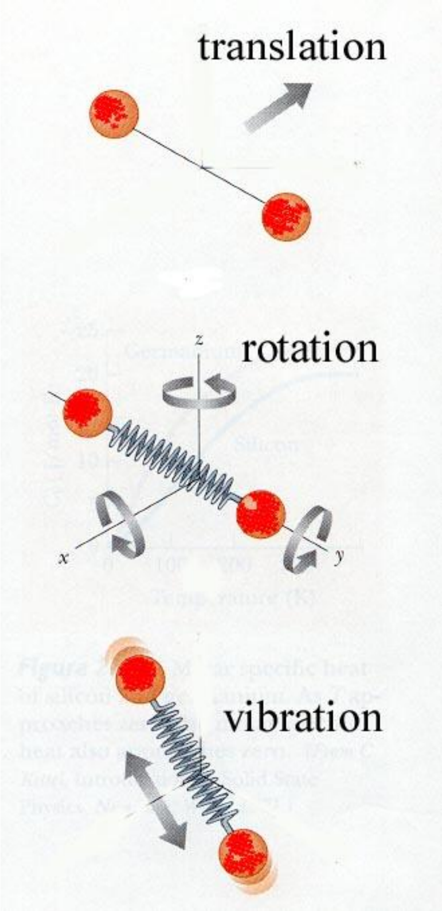
$\Delta U > 0$ is a gain of internal energy

$\Delta U < 0$ is a loss of internal energy

Thermal Energy:
same as internal energy

Vibrational kinetic energy in solids. The hotter the object, the larger the vibrational kinetic energy

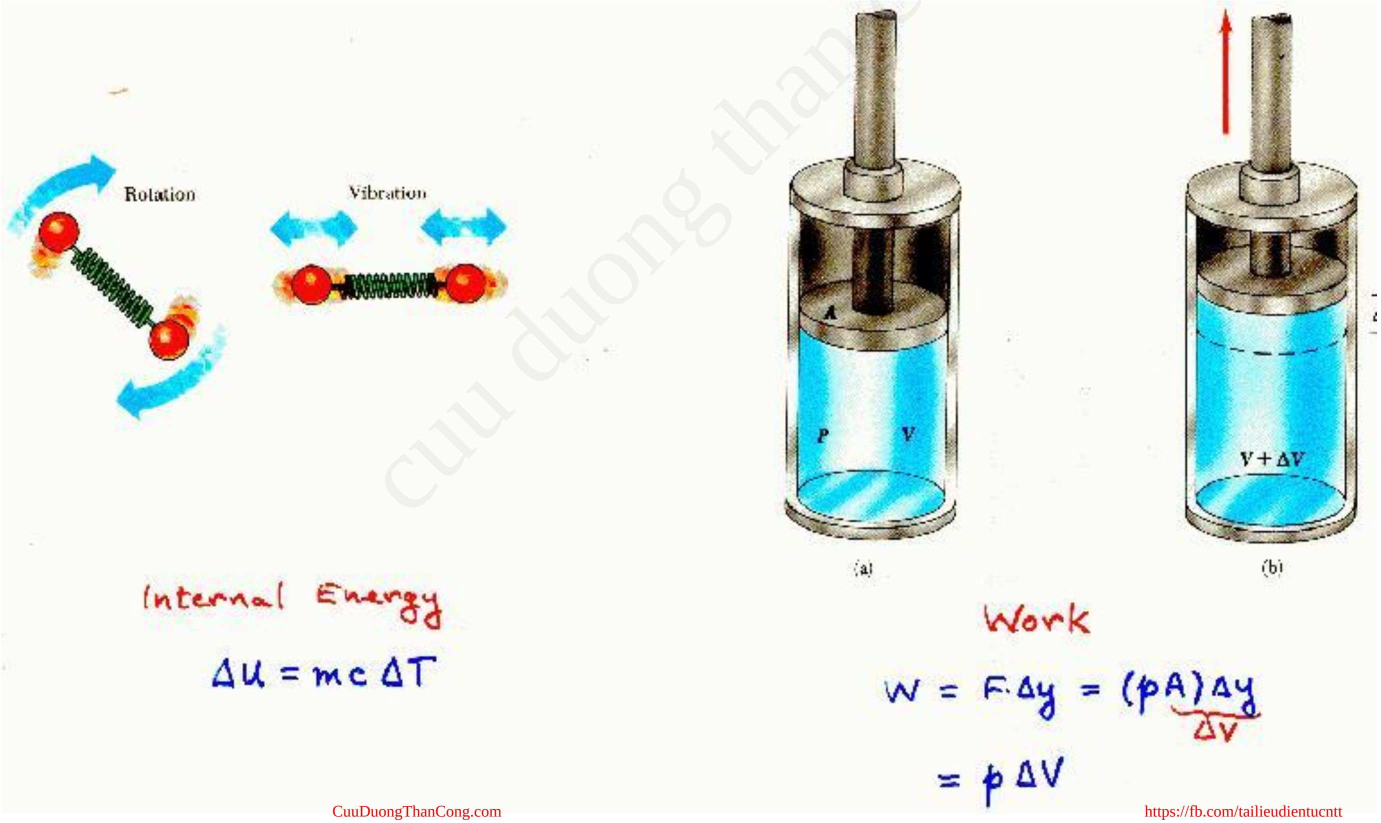




Motions of a diatomic molecule in a fluid

INTERNAL ENERGY (U OR E)

is the total of the kinetic energy due to the motion of molecules (translational, rotational, vibrational) and the potential energy associated with the vibrational and electric energy of atoms within molecules or crystals.



Internal Energy

$\Delta U = mc\Delta T$

Work

$W = F \cdot \Delta y = (pA)\underbrace{\Delta y}_{\Delta V}$

$= p\Delta V$

2.3 INTERNAL ENERGY AND THE FIRST LAW OF THERMODYNAMICS

- One form of work may be converted into another,
- or, work may be converted to heat,
- or, heat may be converted to work,
- but, final energy = initial energy

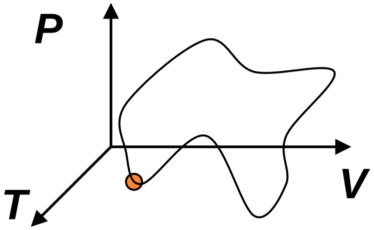
2.3 INTERNAL ENERGY AND THE FIRST LAW OF THERMODYNAMICS

The first law of thermodynamics: the internal energy of a system can be changed by doing work on it or by heating/cooling it.

$$\boxed{\Delta U = Q + W}$$ **conservation of energy.**

Sign convention: we consider ***Q*** and ***W*** to be ***positive*** if energy flows ***into*** the system.

For a cyclic process ($U_i = U_f$) $\Rightarrow$ $Q = - W$.
If, in addition, $Q = 0$ then $W = 0$



An equivalent formulation:

Perpetual motion machines of the first type do not exist.

2.3 INTERNAL ENERGY AND THE FIRST LAW OF THERMODYNAMICS

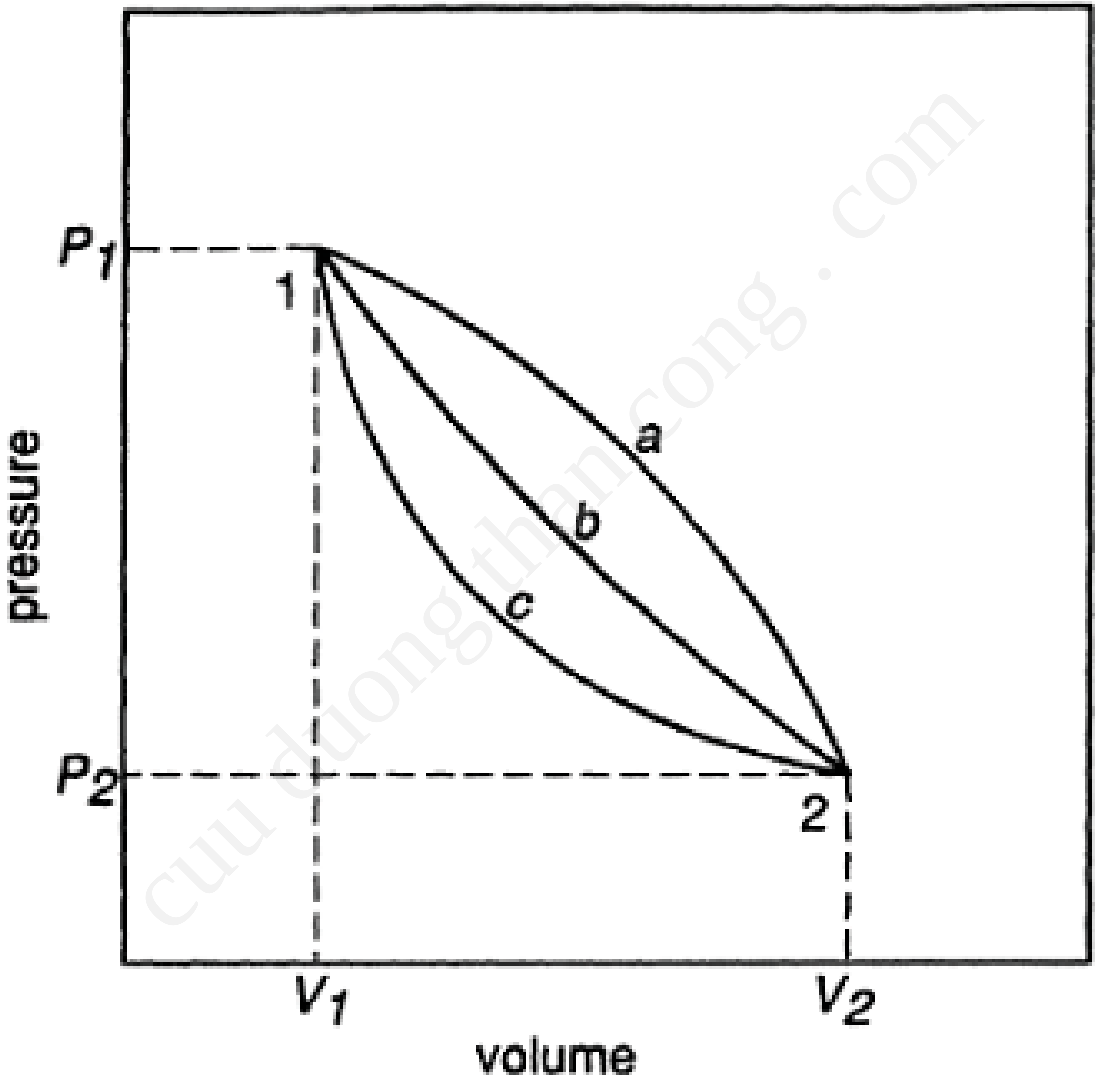
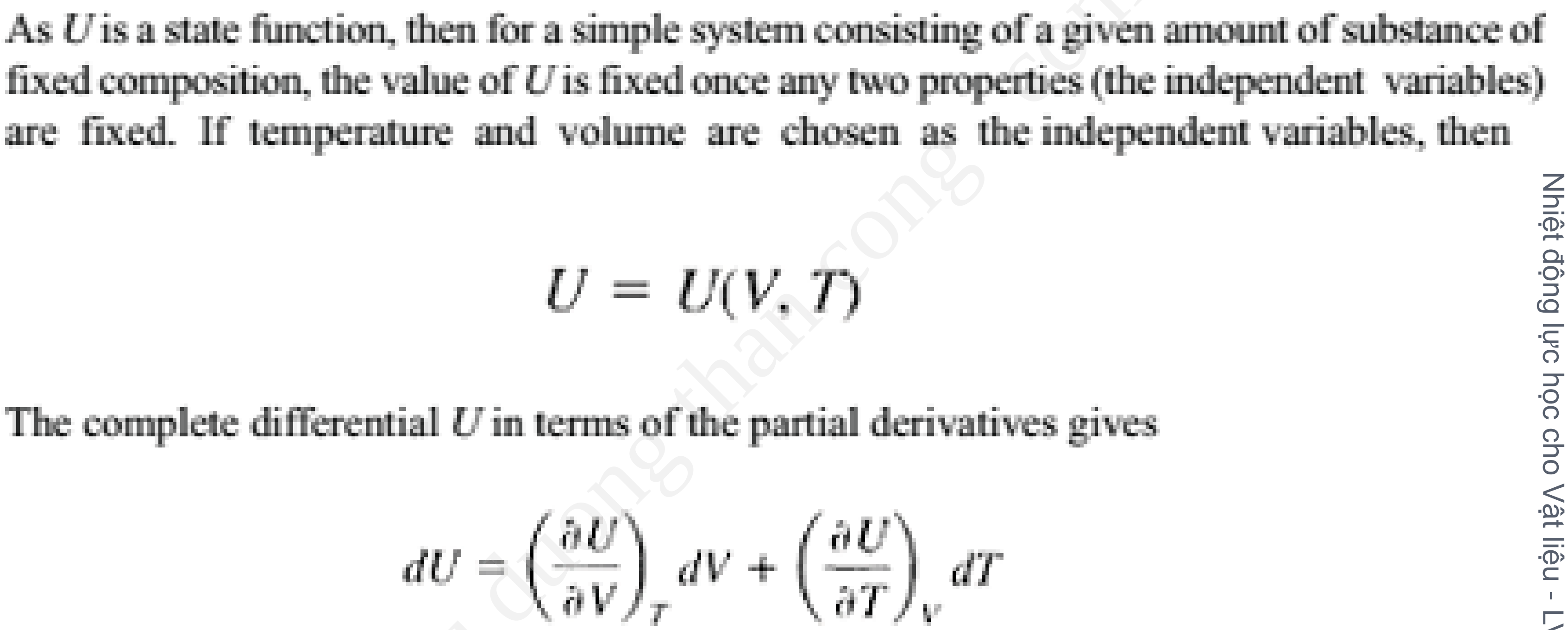


Figure 2.1 Three process paths taken by a fixed quality of gas in moving from the state 1 to the state 2.

2.3 INTERNAL ENERGY AND THE FIRST LAW OF THERMODYNAMICS



As U is a state function, then for a simple system consisting of a given amount of substance of fixed composition, the value of U is fixed once any two properties (the independent variables) are fixed. If temperature and volume are chosen as the independent variables, then

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

The complete differential U in terms of the partial derivatives gives

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

Example,
First Law of Thermodynamics

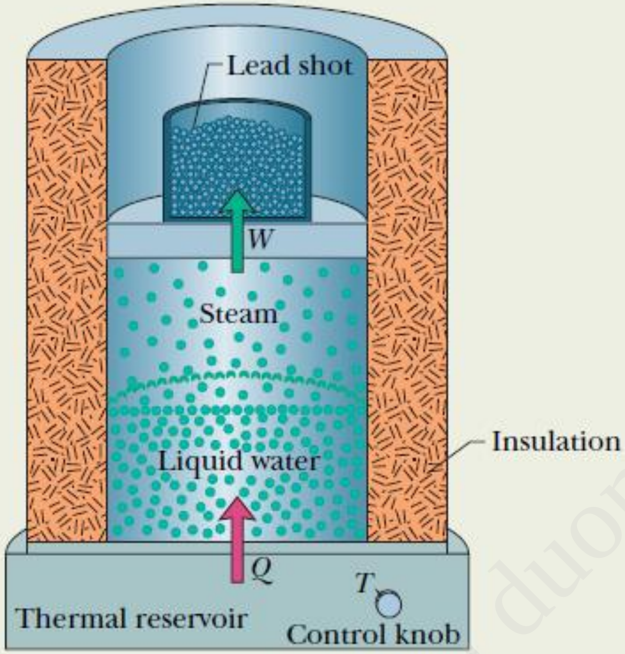


Fig. 18-17 Water boiling at constant pressure. Energy is transferred from the thermal reservoir as heat until the liquid water has changed completely into steam. Work is done by the expanding gas as it lifts the loaded piston.

(b) How much energy is transferred as heat during the process?

KEY IDEA

Because the heat causes only a phase change and not a change in temperature, it is given fully by Eq. 18-16 ($Q = Lm$).

Calculation: Because the change is from liquid to gaseous phase, L is the heat of vaporization L_V, with the value given in Eq. 18-17 and Table 18-4. We find

$$Q = L_V m = (2256 \text{ kJ/kg})(1.00 \text{ kg})$$
$$= 2256 \text{ kJ} \approx 2260 \text{ kJ}. \quad \text{(Answer)}$$

(c) What is the change in the system's internal energy during the process?

KEY IDEA

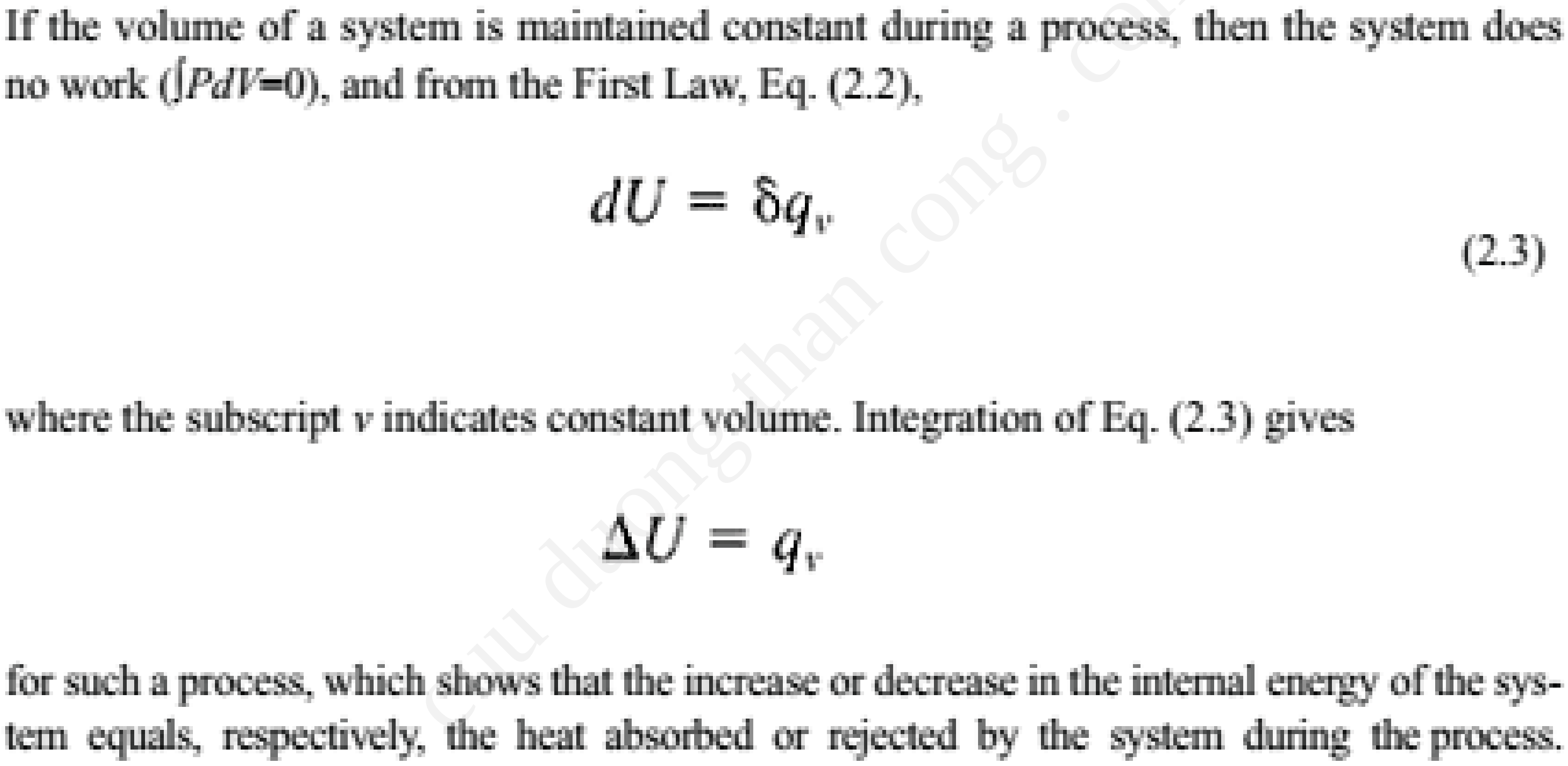
The change in the system's internal energy is related to the heat (here, this is energy transferred into the system) and the work (here, this is energy transferred out of the system) by the first law of thermodynamics (Eq. 18-26).

Calculation: We write the first law as

$$\Delta E_{\text{int}} = Q - W = 2256 \text{ kJ} - 169 \text{ kJ}$$
$$\approx 2090 \text{ kJ} = 2.09 \text{ MJ}. \quad \text{(Answer)}$$

This quantity is positive, indicating that the internal energy of the system has increased during the boiling process. This energy goes into separating the H_2O molecules, which strongly attract one another in the liquid state. We see that, when water is boiled, about 7.5% (= 169 kJ/2260 kJ) of the heat goes into the work of pushing back the atmosphere. The rest of the heat goes into the system's internal energy.

2.4 CONSTANT-VOLUME PROCESSES



If the volume of a system is maintained constant during a process, then the system does no work ($\int PdV=0$), and from the First Law, Eq. (2.2),

$$dU = \delta q_v \tag{2.3}$$

where the subscript *v* indicates constant volume. Integration of Eq. (2.3) gives

$$\Delta U = q_v$$

for such a process, which shows that the increase or decrease in the internal energy of the system equals, respectively, the heat absorbed or rejected by the system during the process.

2.5 CONSTANT-PRESSURE PROCESSES AND THE ENTHALPY *H*

If the pressure is maintained constant during a process which takes the system from state 1 to state 2, then the work done by the system is given as

$$w = \int_1^2 P dV = P \int_1^2 dV = P(V_2 - V_1)$$

and the First Law gives

$$U_2 - U_1 = q_p - P(V_2 - V_1)$$

where the subscript *p* indicates constant pressure. Rearrangement gives

$$(U_2 + PV_2) - (U_1 + PV_1) = q_p$$

and, as the expression *(U+PV)* contains only state functions, the expression itself is a state function. This is termed the *enthalpy, H;* i.e.,

$$H = U + PV \qquad (2.4)$$

Hence, for a constant-pressure process,

$$H_2 - H_1 = \Delta H = q_p \qquad (2.5)$$

Thus the enthalpy change during a constant-pressure process is equal to the heat admitted to or withdrawn from the system during the process.

2.6 HEAT CAPACITY

Before discussing isothermal and adiabatic processes, it is convenient to introduce the concept of heat capacity. The heat capacity, C, of a system is the ratio of the heat added to or withdrawn from the system to the resultant change in the temperature of the system. Thus

$$C = \frac{q}{\Delta T}$$

or if the temperature change is made vanishingly small, then

$$C = \frac{\delta q}{dT}$$

2.6 HEAT CAPACITY

- An increase in internal energy increases the temperature of the medium.
- Different media require different amounts of energy to produce a given temperature change.

2.6 HEAT CAPACITY

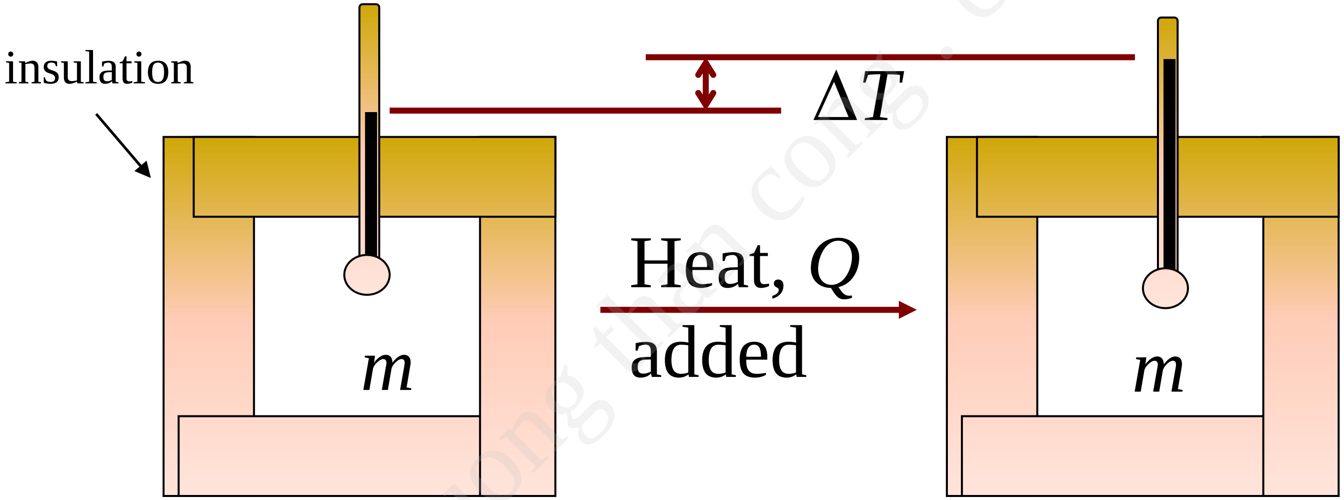
HEAT CAPACITY DEFINED

- Heat capacity: the ratio of heat, Q, needed to change the temperature of a mass, m, by an amount ΔT:

$$C \equiv \frac{Q}{m\Delta T}$$

- Sometimes called specific heat

HEAT CAPACITY FOR CONSTANT VOLUME PROCESSES (C_V)

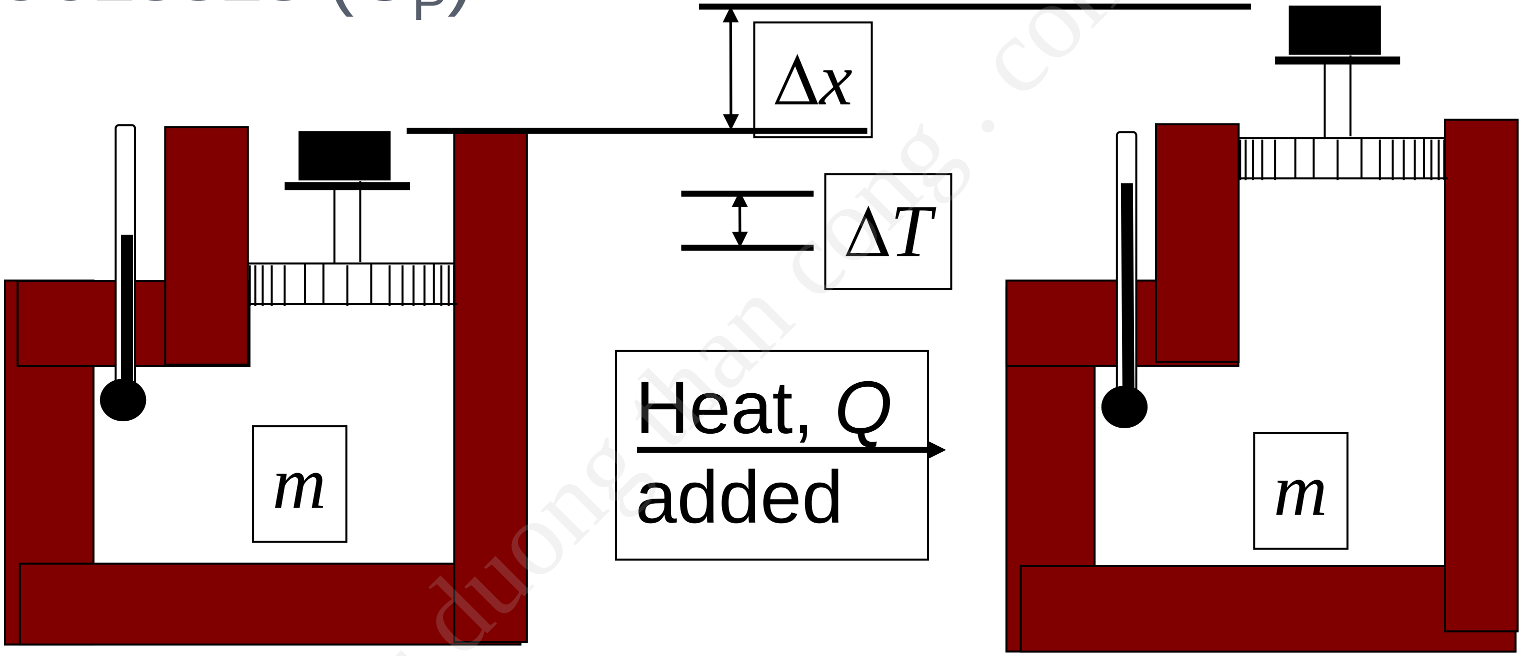


- Heat is added to a substance of mass m in a fixed volume enclosure, which causes a change in internal energy, U. Thus,

$$Q = U_2 - U_1 = \Delta U = m\, C_v\, \Delta T$$

The v subscript implies constant volume

HEAT CAPACITY FOR CONSTANT PRESSURE PROCESSES (C_P)



- Heat is added to a substance of mass m held at a fixed pressure, which causes a change in internal energy, U, AND some PV work.

2.6 HEAT CAPACITY

C_P DEFINED

- Thus,

$$Q = DU + PDV = DH = m\ C_p\ DT$$

The p subscript implies constant pressure

- *Note: H, enthalpy.* is defined as U + PV,

so $dH = d(U+PV) = dU + VdP + PdV$

At constant pressure, $dP = 0$, so

$dH= dU + PdV$

For large changes at constant pressure

$DH = DU + PDV$

2.6 HEAT CAPACITY

EXERCISE

1. Calculate the change in enthalpy per lb_m of nitrogen gas as its temperature decreases from 500 ^oF to 200 ^oF.
2. Two kg of water (C_v=4.2 kJ/kg K) are heated using 200 Btu of energy. What is the change in temperature in K? In ^oF?

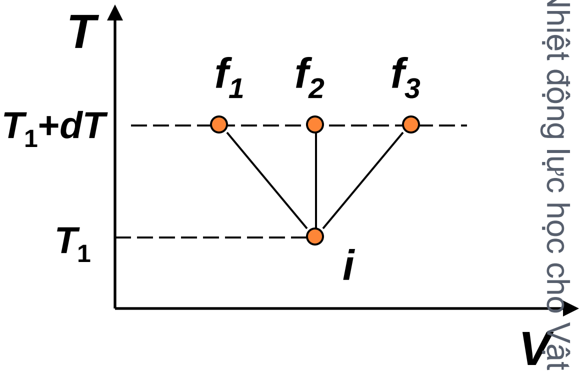
2.6 HEAT CAPACITY

HEAT CAPACITY

The heat capacity of a system - the amount of energy transfer due to heating required to produce a unit temperature rise in that system

$$\boxed{C \equiv \frac{\delta Q}{\Delta T}}$$

C *is NOT a state function* (since ***Q*** is not a state function) – it depends on the path between two states of a system $\Rightarrow$



(isothermic – ***C*** = ∞, adiabatic – ***C*** = 0)

The specific heat capacity $c \equiv \dfrac{C}{m}$

2.6 HEAT CAPACITY

C_V AND C_P

$$\boxed{C = \frac{\delta Q}{dT} = \frac{dU + PdV}{dT}}$$

$\xrightarrow{V = const}$

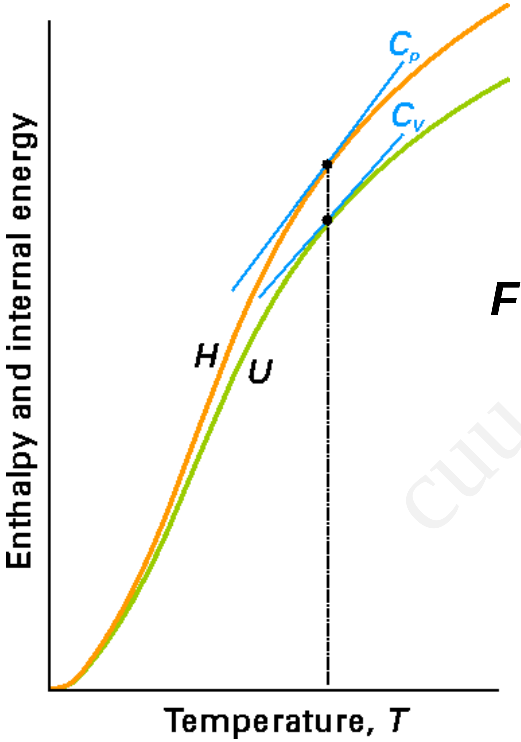
$$\boxed{C_V = \left(\frac{\partial U}{\partial T}\right)_V}$$

the heat capacity at constant volume

$\xrightarrow{P = const}$

$$\boxed{C_P = \left(\frac{\partial H}{\partial T}\right)_P}$$

the heat capacity at constant pressure



To find ***C_P and C_V***, we need ***f* (*P*,*V*,*T*) = 0** and ***U* = *U* (*V*,*T*)**

For an ideal gas $U = \frac{f}{2} N k_B T$ $H = \left(\frac{f}{2} + 1\right) N k_B T$

$$\boxed{C_V = \frac{f}{2} N k_B = \frac{f}{2} nR}$$

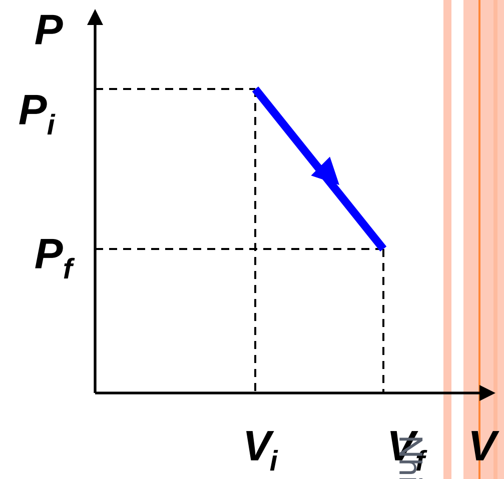
$$\boxed{C_P = \left(\frac{f}{2} + 1\right) nR}$$

# of moles

For one mole of a monatomic ideal gas:

$$\boxed{C_V = \frac{3}{2} R \quad C_P = \frac{5}{2} R}$$

ANOTHER PROBLEM



During the ascent of a meteorological helium-gas filled balloon, its volume increases from $\boldsymbol{V_i} = 1\ \text{m}^3$ to $\boldsymbol{V_f} = 1.8\ \text{m}^3$, and the pressure inside the balloon decreases from 1 bar ($=10^5\ \text{N/m}^2$) to 0.5 bar. Assume that the pressure changes linearly with volume between $\boldsymbol{V_i}$ and $\boldsymbol{V_f}$.

(a) If the initial ***T*** is 300K, what is the final ***T***?

(b) How much work is done ***by*** the gas in the balloon?

(c) How much "heat" does the gas absorb, if any?

$$P(V) = -0.625\,\text{bar/m}^3 \times V + 1.625\,\text{bar}$$

(a) $$PV = Nk_B T \qquad T = \frac{PV}{Nk_B} \qquad T_f = T_i \frac{P_f V_f}{P_i V_i} = 300\text{K}\,\frac{0.5\text{bar}\times 1.8\text{m}^3}{1\text{bar}\times 1\text{m}^3} = 270\text{K}$$

(b) $\delta W_{ON} = -\int_{V_i}^{V_f} P(V)dV$ - work done **on** a system $\delta W_{BY} = \int_{V_i}^{V_f} P(V)dV$ - work done **by** a system

$$\boxed{\delta W_{ON} = -\delta W_{BY}} \quad \delta W_{BY} = \int_{V_i}^{V_f} P(V)dV = \left(0.5\times 0.8\,\text{bar}\cdot\text{m}^3 + 0.5\times 0.4\,\text{bar}\cdot\text{m}^3\right) = 0.6\,\text{bar}\cdot\text{m}^3 = 6\cdot 10^4\,\text{J}$$

(c) $$\Delta U = \delta Q + \delta W_{ON}$$

$$\delta Q = \Delta U - \delta W_{ON} = \frac{3}{2} Nk_B\left(T_f - T_i\right) - W_{ON} = \frac{3}{2} P_i V_i \left(\frac{T_f}{T_i} - 1\right) + \delta W_{BY} = 1.5\cdot 10^5\,\text{J}\times(-0.1) + 6\cdot 10^4\,\text{J} = 4.5\cdot 10^4\,\text{J}$$

2.7 REVERSIBLE ADIABATIC PROCESSES

REVERSIBILITY

- **Reversibility** is the ability to run a process backwards and forwards infinitely without losses.

2.7 REVERSIBLE ADIABATIC PROCESSES

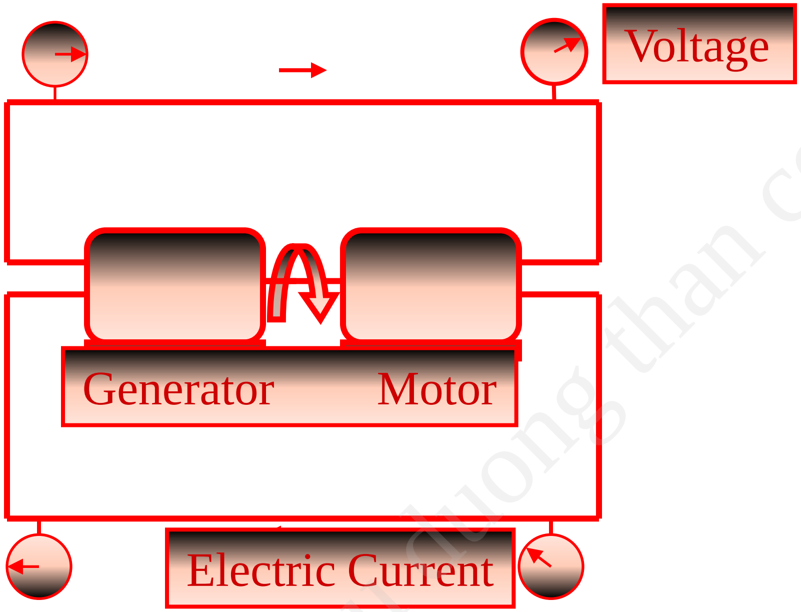
Money analogy

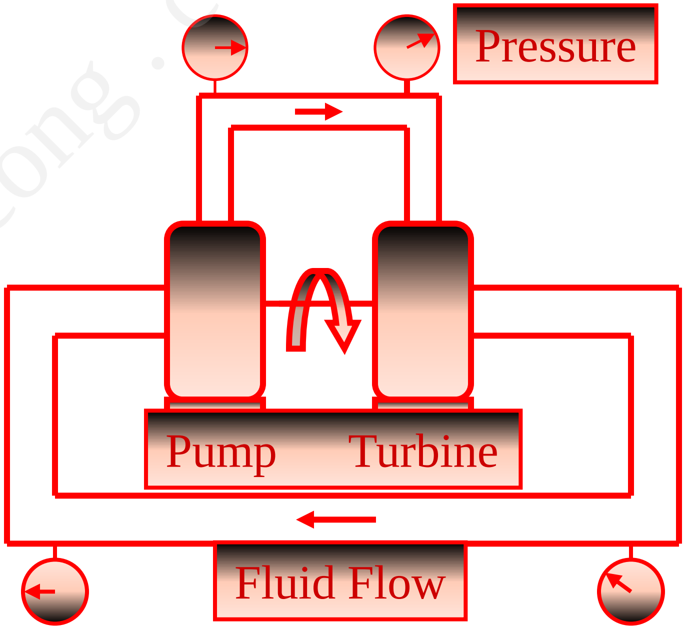
	Reversible (no service fee)		**Irreversible (5% service fee)**	
Day	**Dollars**	**Pounds**	**Dollars**	**Pounds**
Monday	100.00	40.00	100.00	38.00
Tuesday	100.00	40.00	90.25	34.30
Wednesday	100.00	40.00	81.45	30.95
Thursday	100.00	40.00	73.51	27.93
Friday	100.00	40.00	66.34	25.20

Each morning, dollars are converted to pounds.
Each evening, pounds are converted to dollars.

2.7 REVERSIBLE ADIABATIC PROCESSES

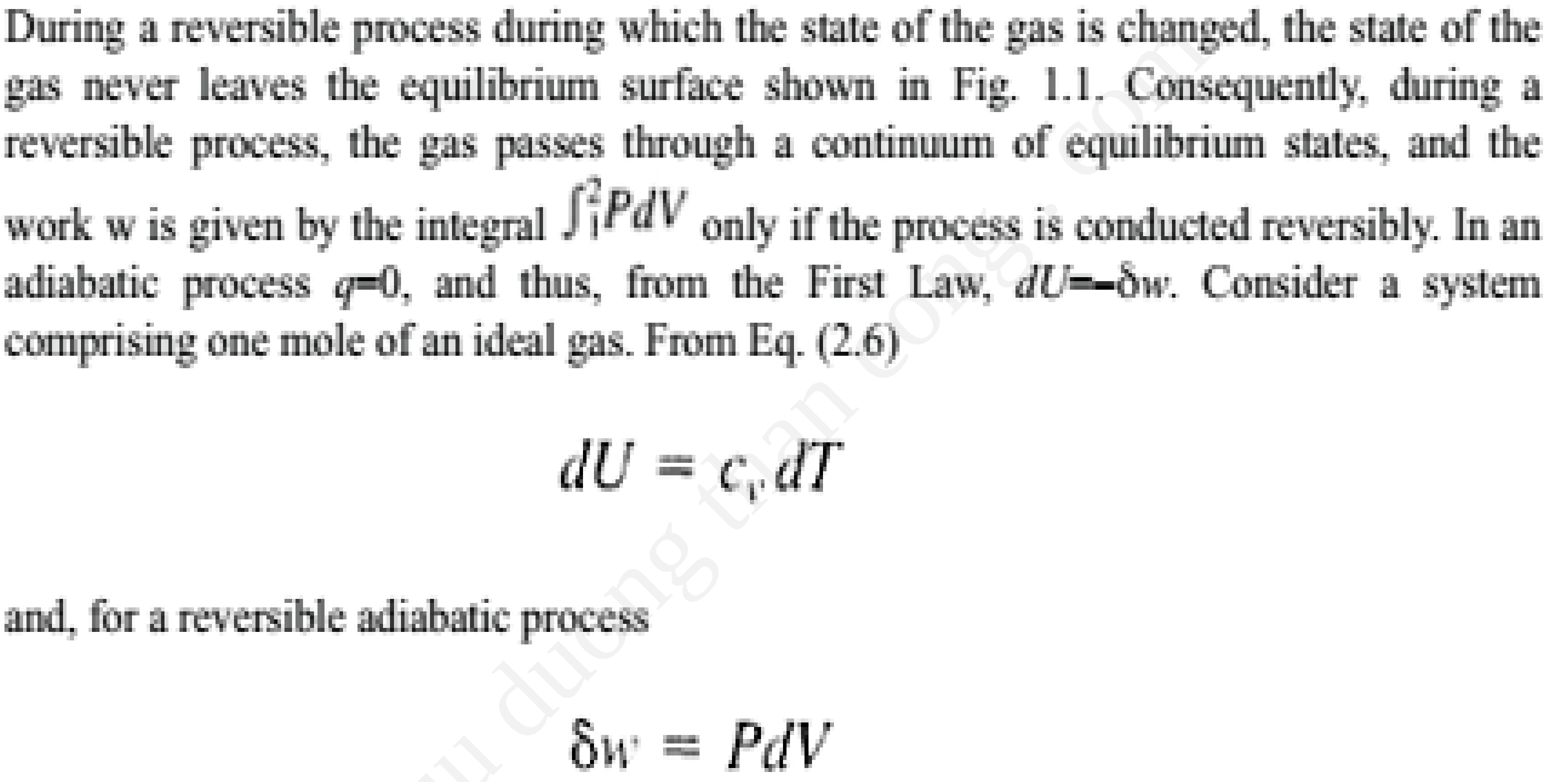
REVERSIBILITY AND ENERGY





- If irreversibilities were eliminated, these systems would run forever.
  - Perpetual motion machines

2.7 REVERSIBLE ADIABATIC PROCESSES



During a reversible process during which the state of the gas is changed, the state of the gas never leaves the equilibrium surface shown in Fig. 1.1. Consequently, during a reversible process, the gas passes through a continuum of equilibrium states, and the work w is given by the integral $\int_1^2 PdV$ only if the process is conducted reversibly. In an adiabatic process $q=0$, and thus, from the First Law, $dU=-\delta w$. Consider a system comprising one mole of an ideal gas. From Eq. (2.6)

$$dU = c_v dT$$

and, for a reversible adiabatic process

$$\delta w = PdV$$

2.7 REVERSIBLE ADIABATIC PROCESSES

Thus

$$c_V\,dT = -P\,dV$$

As the system is one mole of ideal gas, then $P=RT/V$ and hence

$$c_V\,dT = -\frac{RT\,dV}{V}$$

Integrating between states 1 and 2 gives

$$c_V \ln\left(\frac{T_2}{T_1}\right) = R\ln\left(\frac{V_1}{V_2}\right)$$

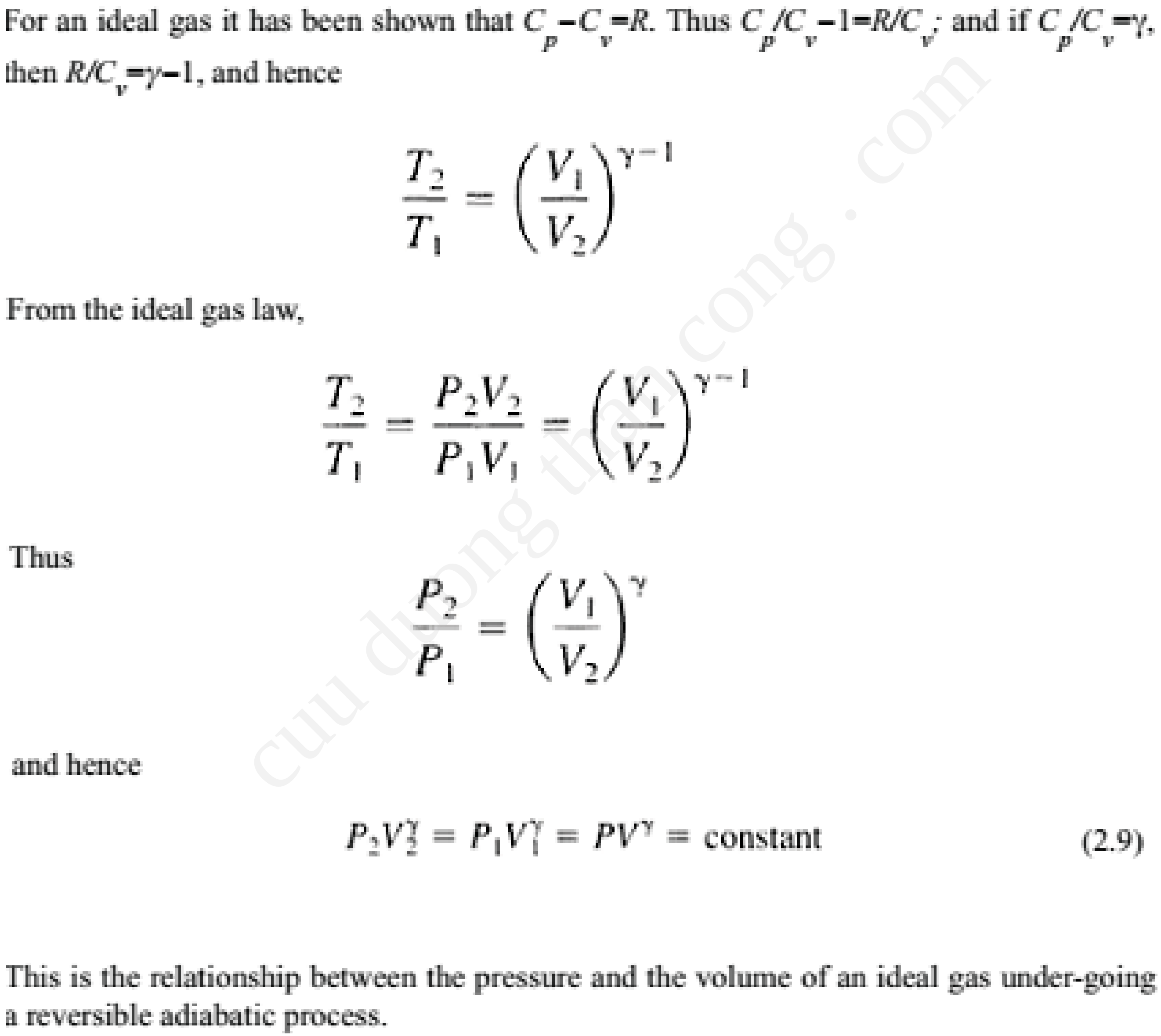
or

$$\left(\frac{T_2}{T_1}\right)^{c_V} = \left(\frac{V_1}{V_2}\right)^{R}$$

or

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{V_1}{V_2}\right)^{R/c_V}$$

2.7 REVERSIBLE ADIABATIC PROCESSES



For an ideal gas it has been shown that $C_p - C_v = R$. Thus $C_p/C_v - 1 = R/C_v$; and if $C_p/C_v = \gamma$, then $R/C_v = \gamma - 1$, and hence

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma - 1}$$

From the ideal gas law,

$$\frac{T_2}{T_1} = \frac{P_2 V_2}{P_1 V_1} = \left(\frac{V_1}{V_2}\right)^{\gamma - 1}$$

Thus

$$\frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^{\gamma}$$

and hence

$$P_2 V_2^{\gamma} = P_1 V_1^{\gamma} = P V^{\gamma} = \text{constant} \qquad (2.9)$$

This is the relationship between the pressure and the volume of an ideal gas under-going a reversible adiabatic process.

2.8 REVERSIBLE ISOTHERMAL PRESSURE OR VOLUME CHANGES OF AN IDEAL GAS

From the First Law

$$dU = \delta q - \delta w$$

and as $dT=0$ (isothermal process), then $dU=0$. Therefore $\delta w=\delta q=PdV= RTdV/V$ per mole of gas.

Integrating between the states 1 and 2 gives

$$w = q = RT\ln\left(\frac{V_2}{V_1}\right) = RT\ln\left(\frac{P_1}{P_2}\right) \tag{2.10}$$

2.8 REVERSIBLE ISOTHERMAL PRESSURE OR VOLUME CHANGES OF AN IDEAL GAS

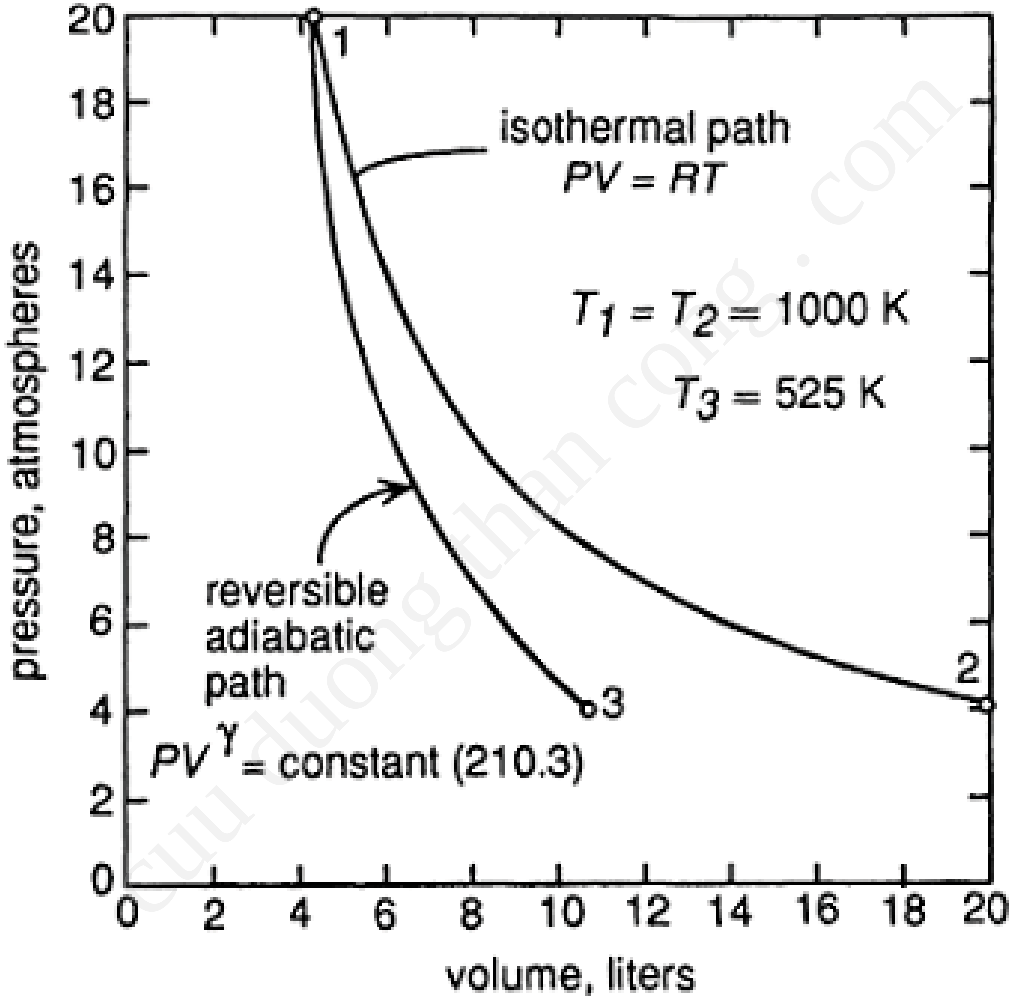


Figure 2.2 Comparison of the process path taken by a reversible isothermal expansion of an ideal gas with the process path taken by a reversible adiabatic expansion of an ideal gas between an initial pressure of 20 atm and a final pressure of 4 atm.

Home work

From 2.1 to 2.8, David Gaskell, p.38-40