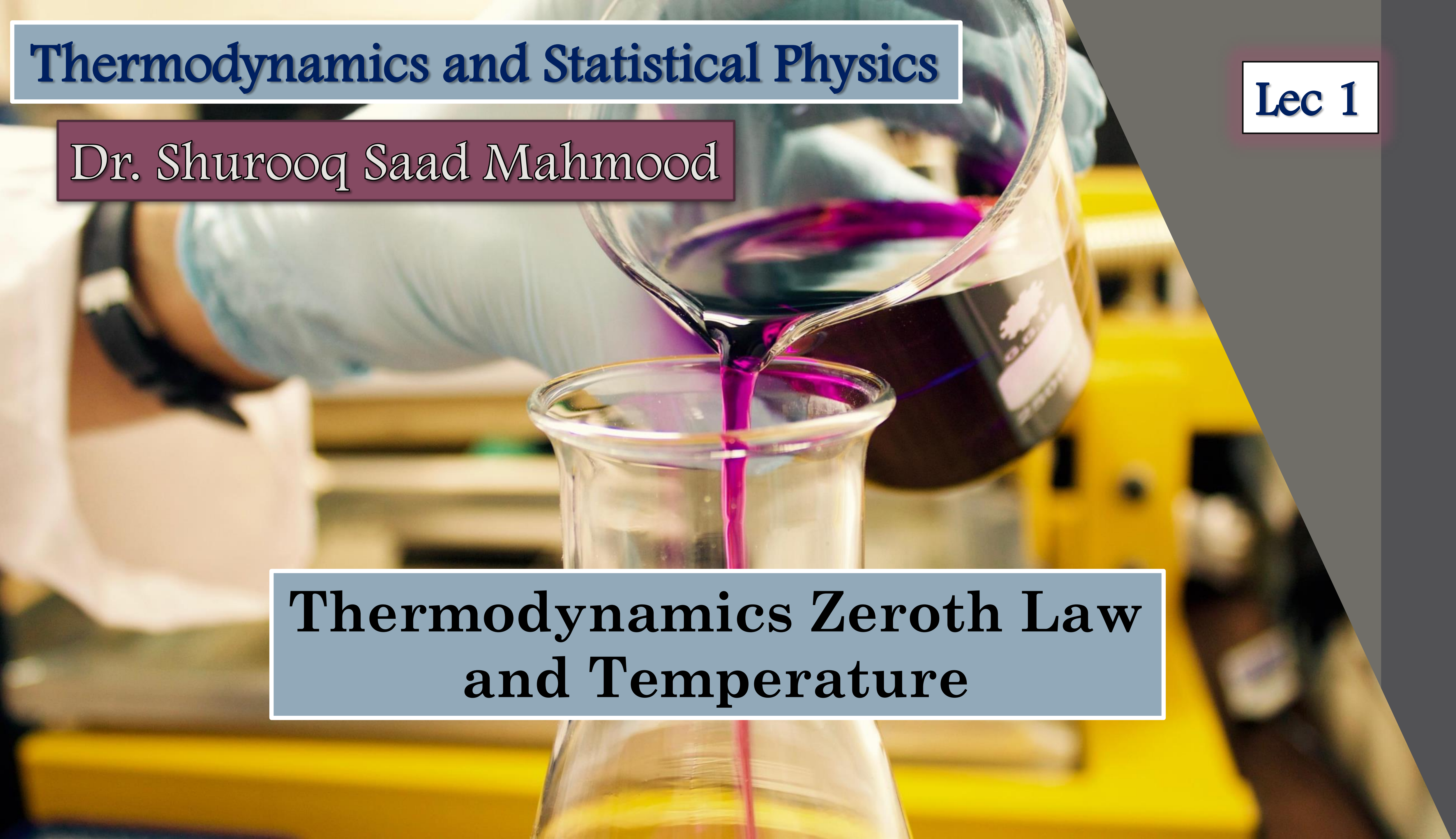


Thermodynamics and Statistical Physics

Dr. Shurooq Saad Mahmood

Lec 1

Thermodynamics Zeroth Law and Temperature

Syllabus

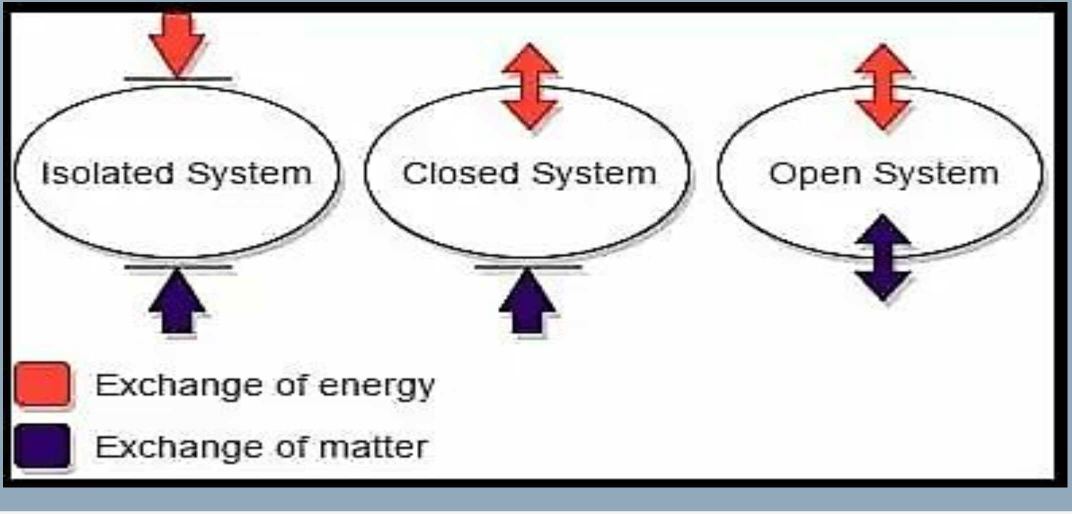
- **Thermodynamics Zeroth Law and Temperature:**
  - Thermodynamics systems.
  - Variables.
  - State equations.
  - Thermometry.
- **First Low of Thermodynamics:**
  - Work.
  - Heat.
  - Phase transformations.
- **Second Low of Thermodynamics:**
  - Irreversible processes.
  - Entropy.
- **Kinetic Theory of Gases.**
- **Introduction to Statistical Mechanics.**

Introduction

- **Thermodynamics** is the branch of physics that **deals with the relationships** between **heat** and **other forms of energy**. In particular, it **describes how thermal energy is converted to and from other forms of energy** and **how it affects matter**.
- **Thermodynamics:** study the situations in which the **temperature** or **state** (solid, liquid, gas) of a system **changes** due to energy transfers. Thermodynamics is very successful in **explaining the bulk properties** of matter and the **correlation** between these **properties** and the **mechanics** of atoms and molecules.

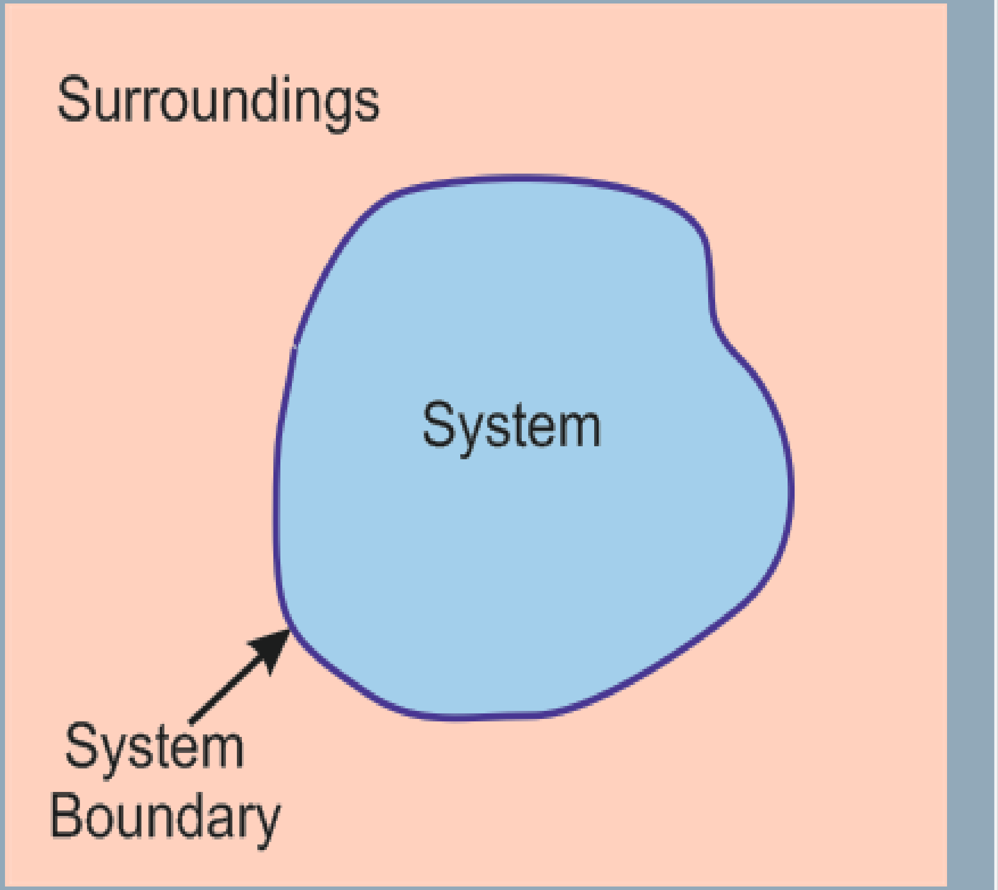
Introduction

- **System:** a **finite quantity of matter** or the **space** which is under thermodynamic study or analysis is called as system. Let us say for example, studying the engine of the vehicle, in this case engine is called as the **system**. Similarly, the other examples of system can be complete refrigerator, air-conditioner, washing machine, heat exchange, a utensil with hot water etc. There are three types of system: **closed system**, **open system** and **isolated system**.



Introduction

- **System Boundary:** the **real or imaginary surface** that **separates** the system from its surroundings is called boundary. The boundary of a system can be **fixed or movable**.
- **Surroundings:** Everything external to the matter or space, which is under thermodynamic study is called surroundings. Between the system and surrounding the exchange of mass or energy or both can occur.
- **Universe :** System and its surroundings together **comprise a Universe**.



Introduction

- **State of the system:** The **present status** of the system **described in terms of properties** such as pressure, temperature, and volume is called the state of system.
- **Properties of the system:** The **characteristics by which the physical condition of the system is described** are called as properties of system. Some examples of these characteristics are: temperature, pressure, volume etc. and are called as **properties of system**. The system properties are of **two types**: **extensive** and **intensive** properties.

Properties of the system

- **Extensive properties of system:**

The properties of the system that **depend on the mass or quantity of the system** are called **extensive properties**. Some examples of extensive properties are: mass, volume, enthalpy, internal energy, entropy etc.

- **Intensive properties of the system:**

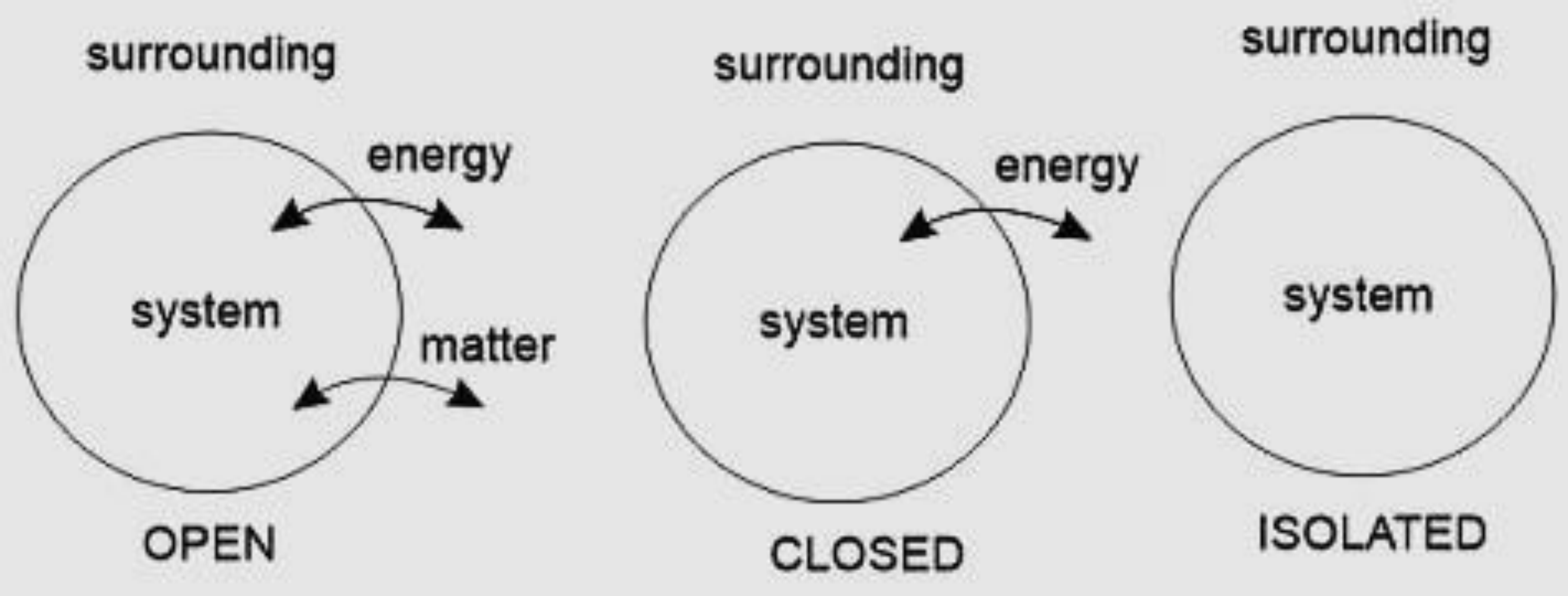
These properties do **not depend on the quantity of matter of the system**. Some of the examples of **intensive properties** are: freezing point temperature, boiling point, temperature of the system, density, specific volume etc.

Types of Thermodynamic Systems

There are three mains types of system: **open system**, **closed system** and **isolated system**. All these have been described below:

1. **Open system**: The system in which the **transfer of mass as well as energy can take place across its boundary** is called as an open system. For example of **engine** is an open system. In this case we provide fuel to engine and it produces power which is given out, thus there is **exchange of mass as well as energy**. The engine also emits heat which is **exchanged with the surroundings**. The other example of open system is **boiling water in an open vessel**, where **transfer of heat as well as mass** in the form of steam takes place between the vessel and surrounding.

Types of Thermodynamic Systems



Types of Thermodynamic Systems

There are three mains types of system: **open system**, **closed system** and **isolated system**. All these have been described below:

2. **Closed system**: The system in which the **transfer of energy takes place across its boundary with the surrounding**, **but** **no transfer of mass takes place** is called as closed system. The closed system is **fixed mass system**. The fluid like air or gas being compressed in the piston and cylinder arrangement is an example of the closed system. In this case the mass of the gas remains constant but it can get heated or cooled. Another example is the water being heated in the closed vessel, where water will **get heated** but its mass will remain same.

Types of Thermodynamic Systems

There are three mains types of system: **open system**, **closed system** and **isolated system**. All these have been described below:

3. **Isolated system**: The system in which **neither the transfer of mass nor that of energy takes place across its boundary with the surroundings** is called as isolated system. For example if the piston and cylinder arrangement in which the fluid like air or gas is being compressed or expanded is **insulated** it becomes isolated system. Here there will neither transfer of mass nor that of energy. Similarly hot water, coffee or tea kept in the thermos flask is closed system. However, if we pour this fluid in a cup, it becomes an open system.

Thermodynamics Zeroth Law and Temperature

We often associate the concept of temperature with how hot or cold an object feels when we touch it. In this way, our senses provide us with **a qualitative indication of temperature**. Our senses, however, are unreliable and often mislead us.

Skin measures the rate of energy transfer by heat rather than the actual temperature. What we need is a reliable and reproducible method for measuring the relative hotness or coldness of objects rather than the rate of energy transfer. Scientists have developed a variety of thermometers for making such quantitative measurements.

When hot water and cold water are mixed in a cup, the final temperature of the mixture is somewhere between the initial hot and cold temperatures.

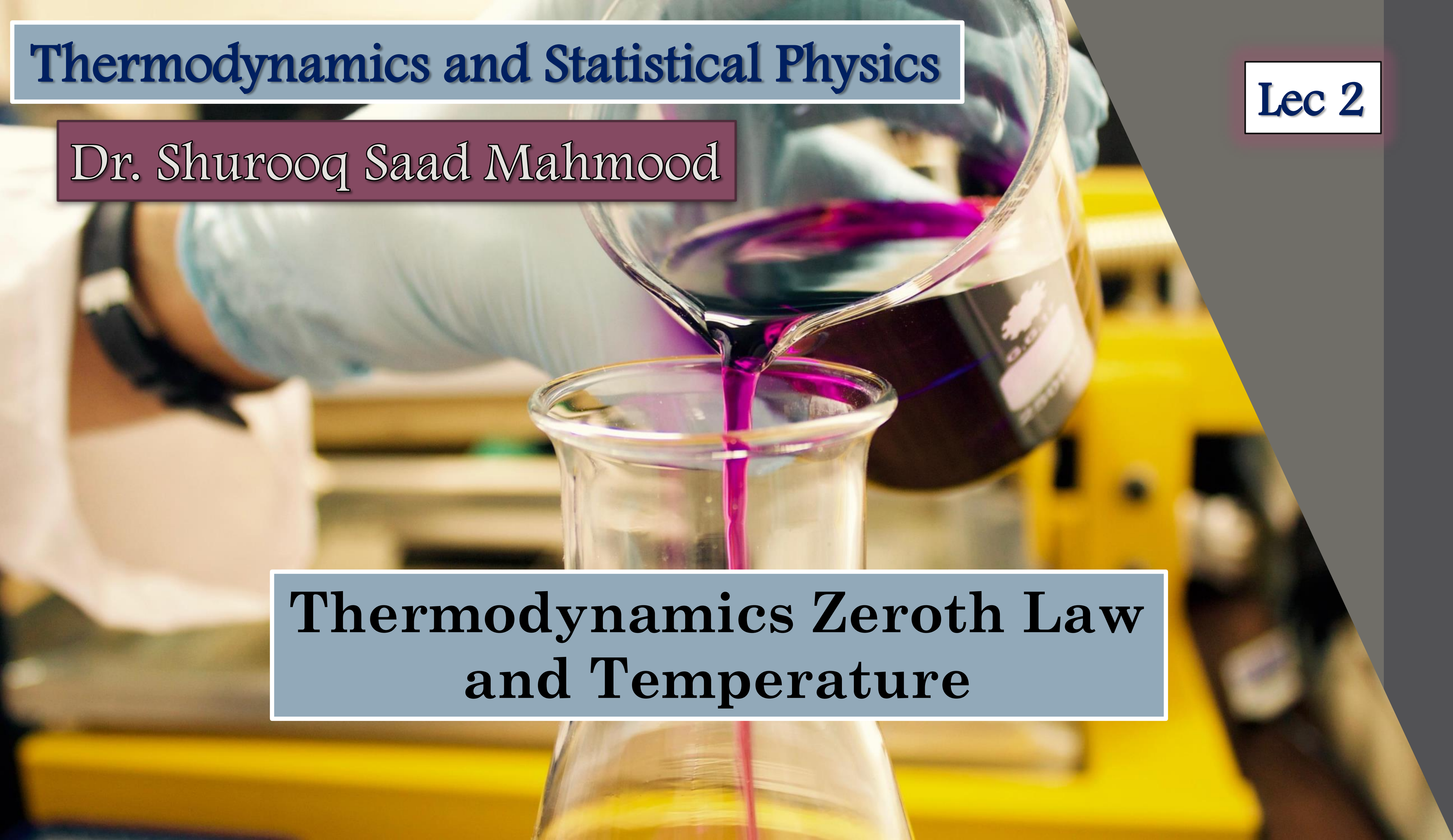
we assume that two objects are in **thermal contact** with each other if **energy can be exchanged between them** by these processes due to a **temperature difference**.

Thermal equilibrium is a situation in which two objects would **not exchange energy by heat or electromagnetic radiation** if they were **placed in thermal contact**.

Thermodynamics and Statistical Physics

Dr. Shurooq Saad Mahmood

Lec 2



Thermodynamics Zeroth Law and Temperature

Thermal Contact and Thermal Equilibrium

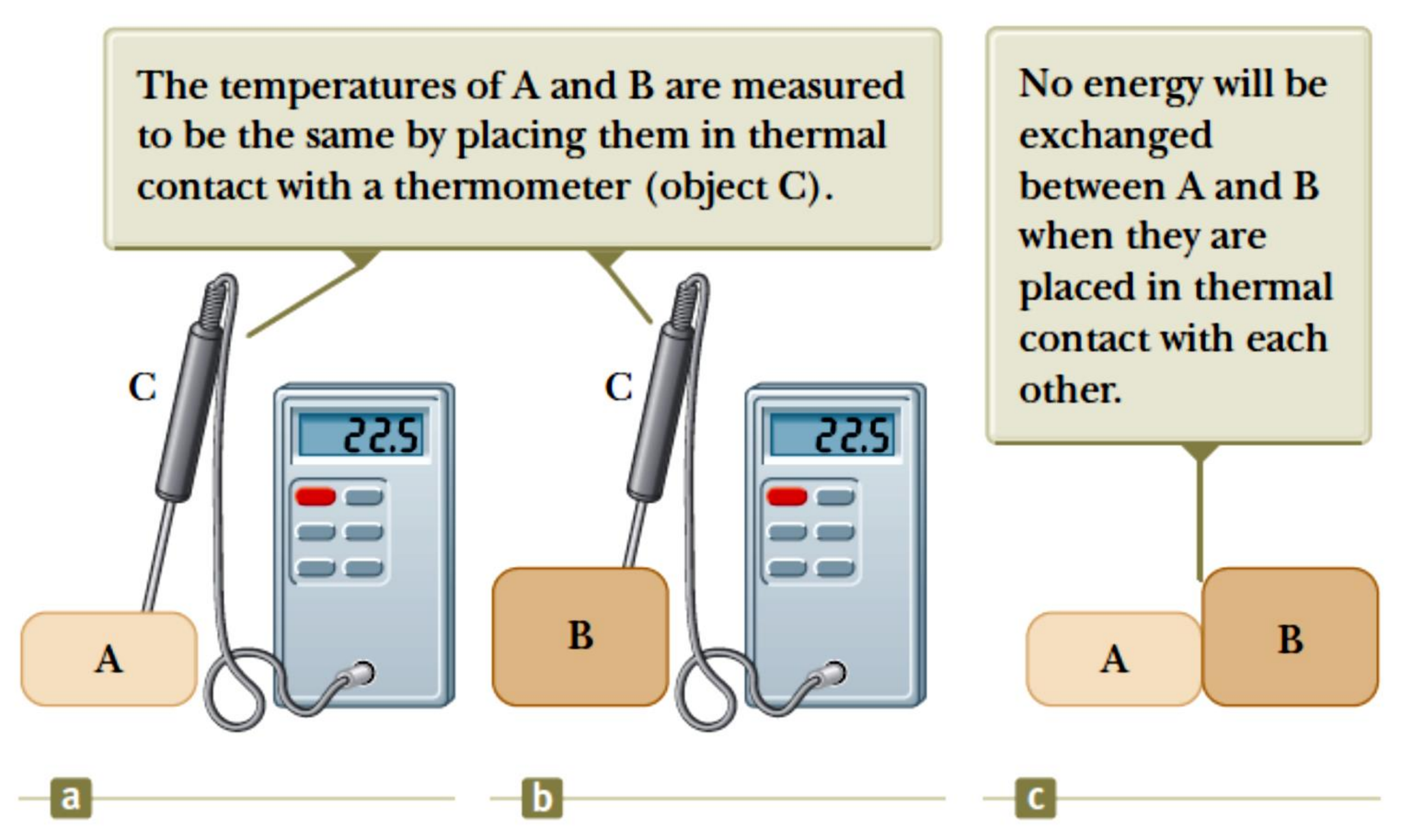
let’s assume that two objects are in **thermal contact** with each other if **energy can be exchanged between them** by these processes due to a **temperature difference**.

Thermal equilibrium is a situation in which two objects would **not exchange energy by heat or electromagnetic radiation** if they were **placed in thermal contact**.

Thermal Contact and Thermal Equilibrium

Let’s consider two objects A and B, which are not in thermal contact, and a third object C, which is our **thermometer**. We wish to determine whether A and B are in thermal equilibrium with each other. The **thermometer** (object C) is first placed in thermal contact with object A until thermal equilibrium is reached as shown in Figure (1a). From that moment on, the thermometer’s reading remains constant and we record this reading. The **thermometer** is then removed from object A and placed in thermal contact with object B as shown in Figure (1b). The reading is again recorded after thermal equilibrium is reached. If the two readings are the same, we can conclude that object A and object B are in thermal equilibrium with each other. If they are placed in contact with each other as in Figure (1c), there is no exchange of energy between them.

Thermal Contact and Thermal Equilibrium


The temperatures of A and B are measured to be the same by placing them in thermal contact with a thermometer (object C).

No energy will be exchanged between A and B when they are placed in thermal contact with each other.

Figure (1): The zeroth law of thermodynamics.

Zeroth law of thermodynamics

We can summarize these results in a statement known as the **zeroth law of thermodynamics (the law of equilibrium):**

If objects A and B are separately in thermal equilibrium with a third object C, then A and B are in thermal equilibrium with each other.

- This statement can easily be proved experimentally and is very important because it enables us to define temperature. Temperature is the property that determines whether an object is in thermal equilibrium with other objects.

Temperature

Temperature can be thought of as the property that determines whether an object is in thermal equilibrium with other objects.

Two objects in thermal equilibrium with each other are at the same temperature.

Conversely, if two objects have different temperatures, they are not in thermal equilibrium with each other. We now know that temperature is something that determines whether or not energy will transfer between two objects in thermal contact.

Thermometers and the Celsius Temperature Scale

Thermometers are devices that are used to measure the temperature of a system.

- All thermometers are based on the principle that some physical property of a system changes as the system's temperature changes.

Some physical properties that change with temperature are:

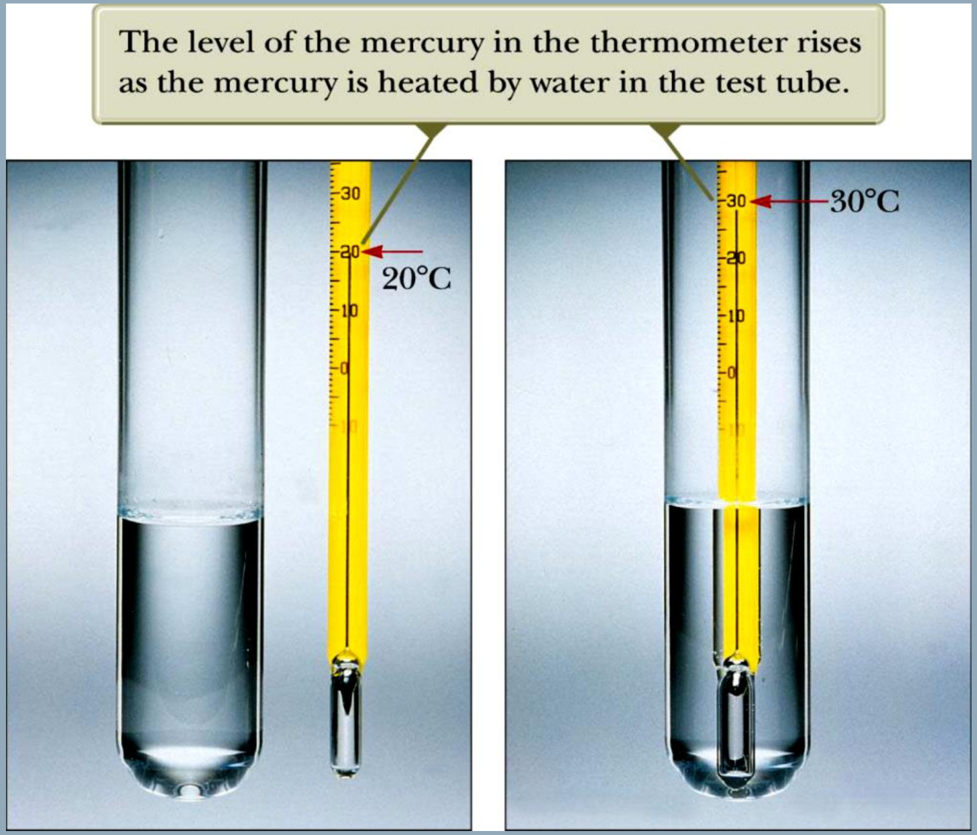
(1) The volume of a liquid.
(2) The dimensions of a solid.
(3) The pressure of a gas at constant volume.
(4) The volume of a gas at constant pressure.
(5) The electric resistance of a conductor.
(6) The color of an object.

Thermometers and the Celsius Temperature Scale

A common **thermometer** in everyday use **consists** of a mass of liquid -usually *mercury* or *alcohol*- that expands into a glass capillary tube when **heated**.

In this case, the physical property that changes is the volume of a liquid.

Any temperature change in the range of the thermometer can be defined as being proportional to the change in length of the liquid column.


The level of the mercury in the thermometer rises as the mercury is heated by water in the test tube.

Thermometers and the Celsius Temperature Scale

The thermometer can be calibrated by placing it in thermal contact with some natural systems that remain at constant temperature.

One such system is a mixture of water and ice in thermal equilibrium at atmospheric pressure.

This mixture is defined to have a temperature of zero degrees Celsius, which is written as 0°C; this temperature is called the ***ice point*** of water.

Another commonly used system is a mixture of water and steam in thermal equilibrium at atmospheric pressure; its temperature is 100°C, which is the ***steam point*** of water.

Thermometers and the Celsius Temperature Scale

The liquid levels in the thermometer have been established at these two points, the length of the liquid column between the two points is **divided** into 100 equal segments to create the Celsius scale. Thus, each segment denotes a change in temperature of one Celsius degree.

A mercury thermometer, for example, **cannot** be used **below the freezing point of mercury, which is -39°C**, and an alcohol thermometer is **not useful** for measuring temperatures **above 85°C, the boiling point of alcohol**.

The Constant-Volume Gas Thermometer and the Absolute Temperature Scale

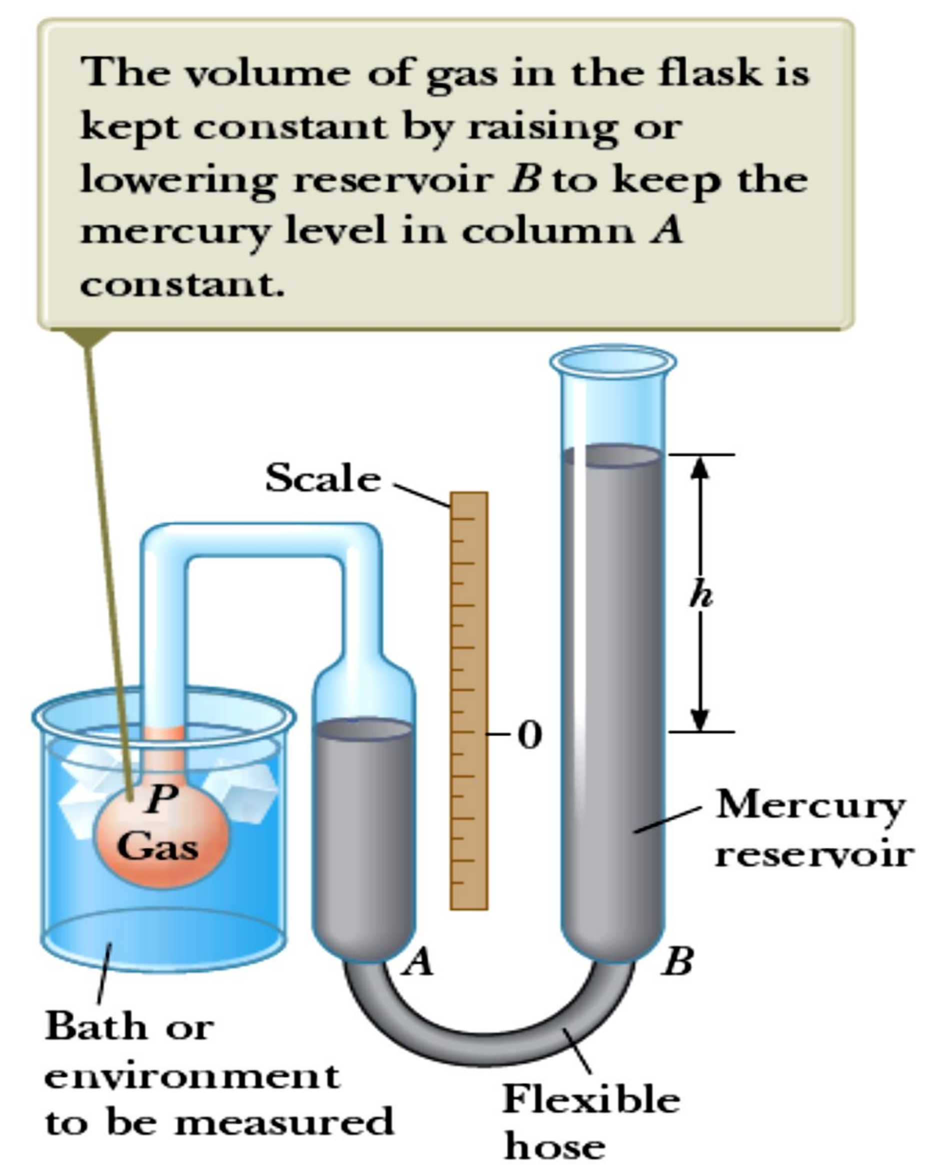
The physical change in this device is the variation of pressure of a fixed volume of gas with temperature.

How to calibrate this device ?

**The flask was immersed in an ice water bath, and mercury reservoir B was raised or lowered until the top of the mercury in column A was at the zero point on the scale.

The ***height h*, the difference between the mercury levels in reservoir B and column A, indicated the pressure in the flask at 0°C.

The Constant-Volume Gas Thermometer and the Absolute Temperature Scale



The volume of gas in the flask is kept constant by raising or lowering reservoir *B* to keep the mercury level in column *A* constant.

Figure (2): A constant-volume gas thermometer measures the pressure of the gas contained in the flask immersed in the bath.

The Constant-Volume Gas Thermometer and the Absolute Temperature Scale

**The flask was then immersed in water at the steam point, and reservoir B was readjusted until the top of the mercury in column A was again at zero on the scale.

**This adjustment of reservoir B gave a value for the gas pressure at 100°C.

**These two pressure and temperature values were then plotted, as shown in Figure (3). The line connecting the two points serves as a calibration curve for unknown temperatures.

The Constant-Volume Gas Thermometer and the Absolute Temperature Scale

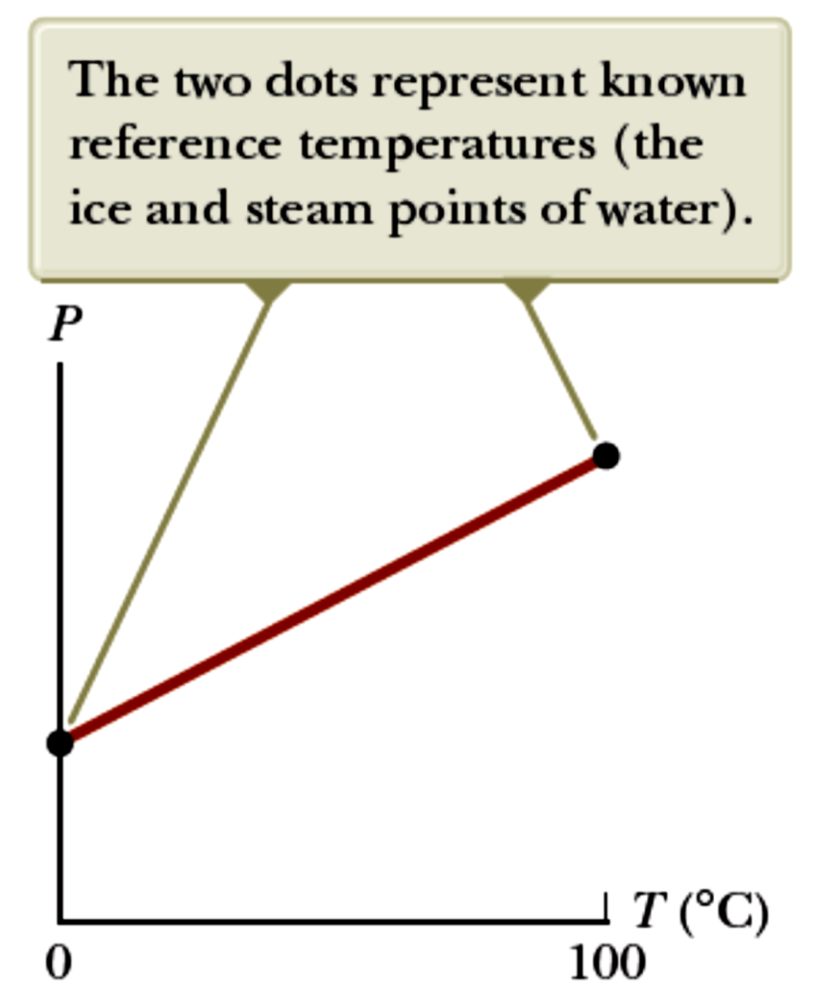
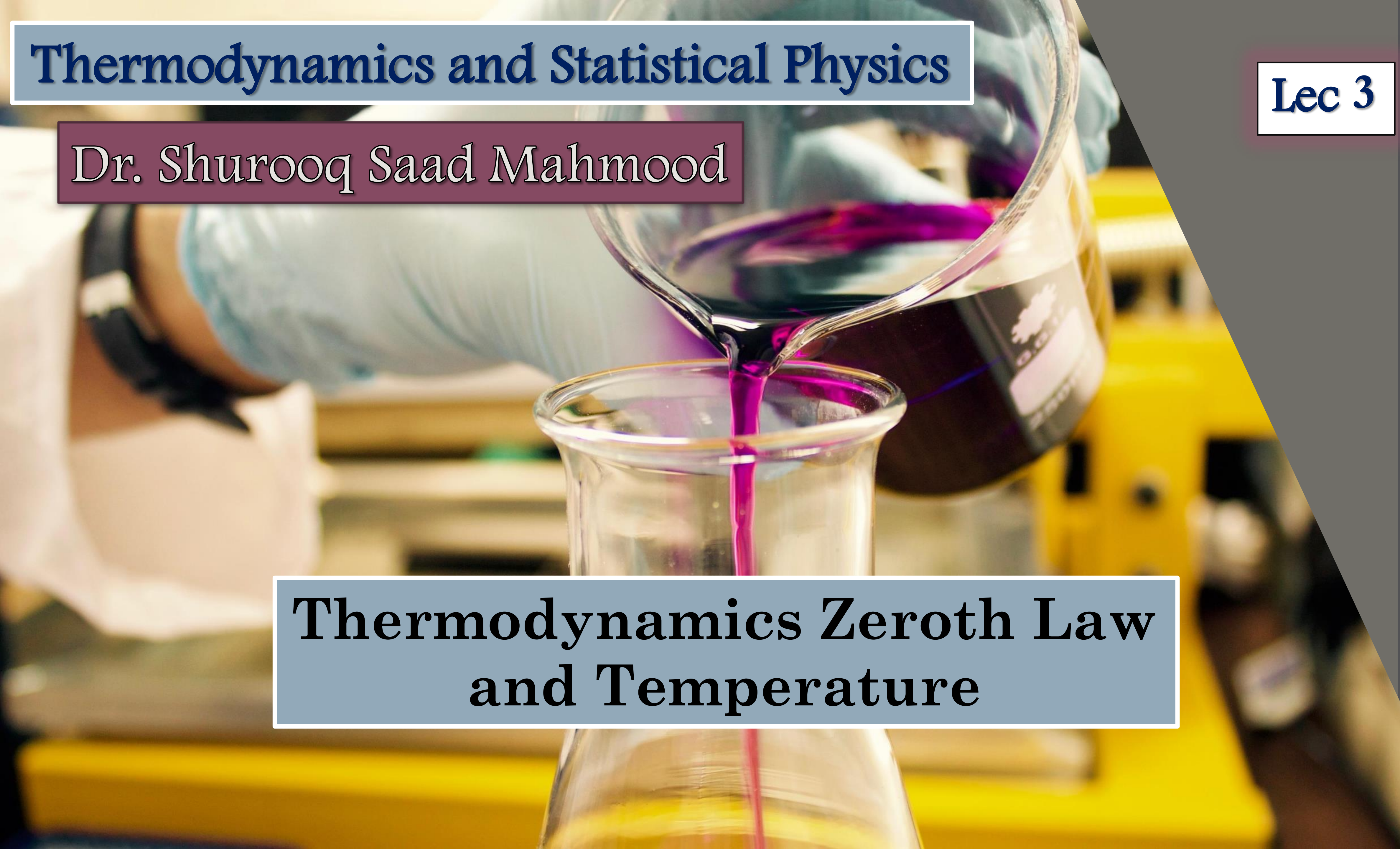


Figure (3): A typical graph of pressure versus temperature taken with a constant-volume gas thermometer.



Thermodynamics and Statistical Physics

Dr. Shurooq Saad Mahmood

Lec 3

Thermodynamics Zeroth Law and Temperature

The Constant-Volume Gas Thermometer and the Absolute Temperature Scale

The physical change in this device is the variation of pressure of a fixed volume of gas with temperature.

How to calibrate this device ?

**The flask was immersed in an ice water bath, and mercury reservoir B was raised or lowered until the top of the mercury in column A was at the zero point on the scale.

The ***height h*, the difference between the mercury levels in reservoir B and column A, indicated the pressure in the flask at 0°C.

The Constant-Volume Gas Thermometer and the Absolute Temperature Scale

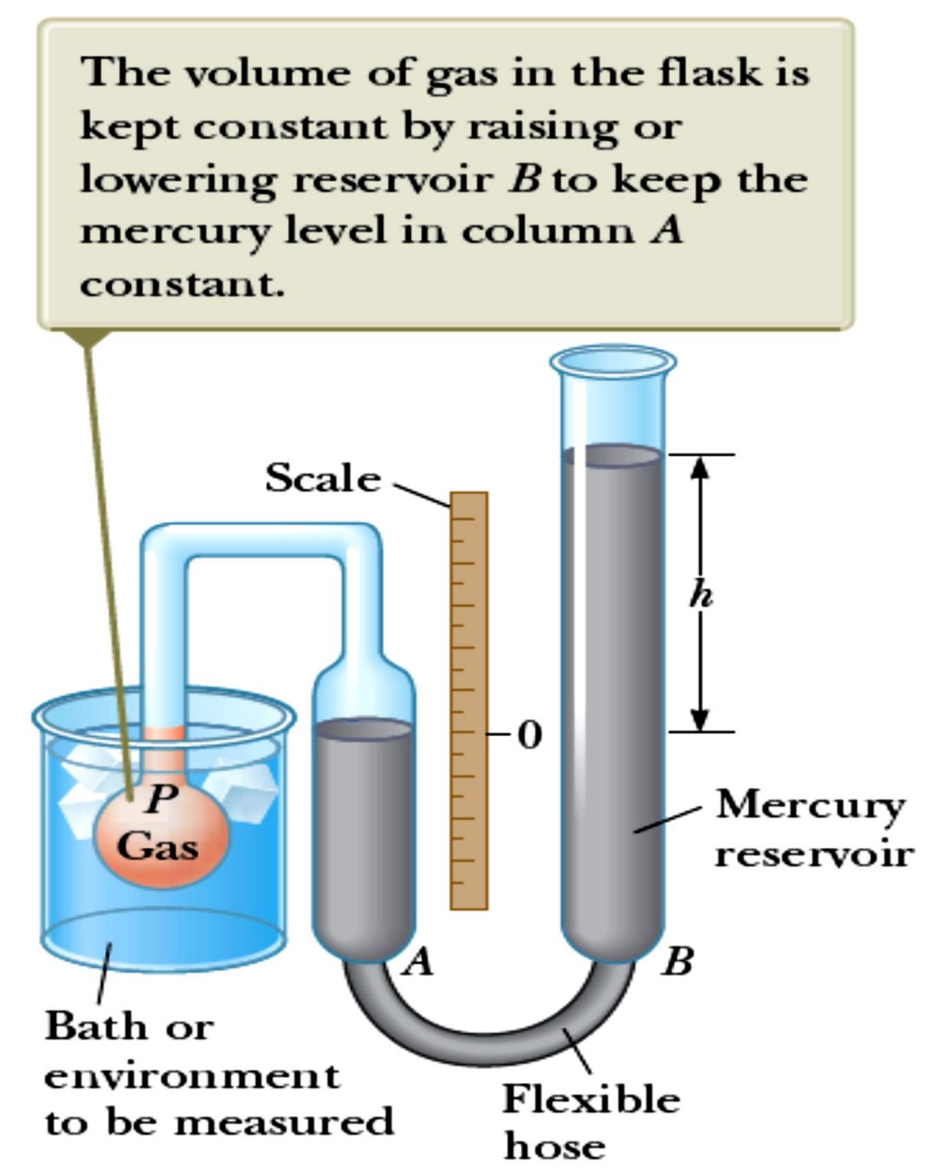


Figure (2): A constant-volume gas thermometer measures the pressure of the gas contained in the flask immersed in the bath.

The Constant-Volume Gas Thermometer and the Absolute Temperature Scale

**The flask was then immersed in water at the steam point, and reservoir B was readjusted until the top of the mercury in column A was again at zero on the scale.

**This adjustment of reservoir B gave a value for the gas pressure at 100°C.

**These two pressure and temperature values were then plotted, as shown in Figure (3). The line connecting the two points serves as a calibration curve for unknown temperatures.

The Constant-Volume Gas Thermometer and the Absolute Temperature Scale

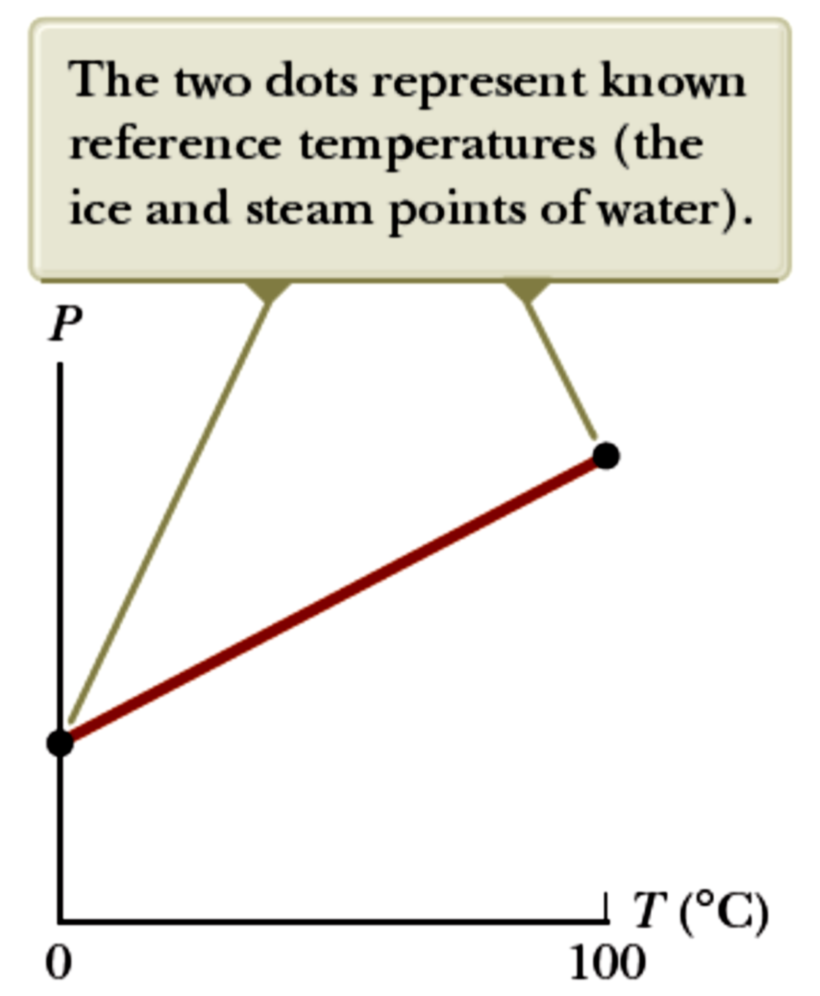


Figure (3): A typical graph of pressure versus temperature taken with a constant-volume gas thermometer.

The Constant-Volume Gas Thermometer and the Absolute Temperature Scale

Experiments show that the **thermometer readings** are nearly **independent** of the type of gas used, as long as the gas pressure is low and the temperature is well above the point at which the gas liquefies Figure (4). The agreement among thermometers using various gases **improves** as the pressure is reduced.

If we extend the straight lines in Figure (4) toward negative temperatures, we find a remarkable result—in every case, **the pressure is zero** when **the temperature is -273.15°C**!

This temperature is often referred to as **absolute zero**.

The conversion between the **absolute temperature** scale and **Celsius scale** is:

$$T_{\mathrm{C}} = T - 273.15 \qquad \text{……………….. (1)}$$

where $\boldsymbol{T_c}$ is the **Celsius temperature** and $\boldsymbol{T}$ is the **absolute temperature**.

The Constant-Volume Gas Thermometer and the Absolute Temperature Scale

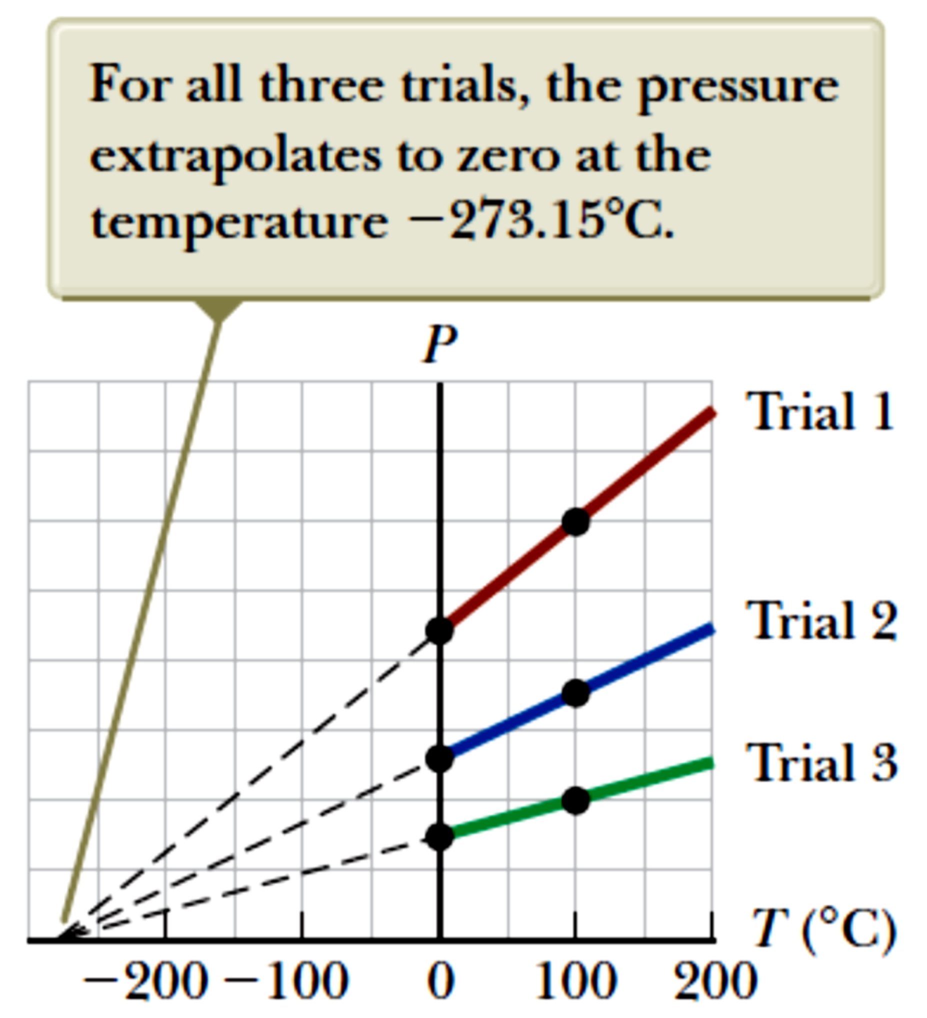

For all three trials, the pressure extrapolates to zero at the temperature −273.15°C.

Figure (4): Pressure versus temperature for experimental trials in which gases have different pressures in a constant-volume gas thermometer.

Absolute Temperature Scale

Because the ice and steam points are experimentally difficult to duplicate and depend on atmospheric pressure, an **absolute temperature scale based on two new fixed points** was adopted in 1954 by the International Committee on Weights and Measures. The **first point is absolute zero**. The **second** reference temperature for this new scale was chosen as **the triple point of water**, which is the single combination of temperature and pressure at which liquid water, gaseous water, and ice (solid water) coexist in equilibrium.

This **triple point** occurs at **a temperature of 0.01°C** and **a pressure of 4.58 mm of mercury**. On the new scale, which **uses the unit kelvin**, the **temperature of water at the triple point was set at 273.16 kelvins**, abbreviated 273.16 K.

The Celsius, Fahrenheit, and Kelvin Temperature Scales

Equation (1) shows that the **Celsius temperature** T_C is **shifted** from the **absolute (Kelvin) temperature** T by **273.15°**. Because the size of one degree is the same on the two scales, a temperature difference of 5°C is equal to a temperature difference of 5 K. The two scales **differ only in the choice of the zero point**. Therefore, the ice-point temperature on the Kelvin scale, 273.15 K, corresponds to 0.00°C, and the Kelvin-scale steam point, 373.15 K, is equivalent to 100.00°C.

A common temperature scale in everyday use in the United States is the **Fahrenheit scale**. This scale sets the temperature of the ice point at 32°F and the temperature of the steam point at 212°F. The relationship between the **Celsius and Fahrenheit temperature scales** is

$$T_{\mathrm{F}} = \tfrac{9}{5}T_{\mathrm{C}} + 32^\circ\mathrm{F} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

The Celsius, Fahrenheit, and Kelvin Temperature Scales

We can use Equations (1) and (2) to find a **relationship between changes in temperature on the Celsius, Kelvin, and Fahrenheit scales**:

$$\Delta T_C = \Delta T = \tfrac{5}{9}\Delta T_F \qquad \text{……………..} \ (3)$$

Example 1: Converting Temperatures

On a day when the temperature reaches 50°F, what is the temperature in degrees Celsius and in kelvins?

Solution

Solve Eq. (2) for the Celsius temperature and substitute numerical values:

$$T_C = \tfrac{5}{9}(T_F - 32) = \tfrac{5}{9}(50 - 32) = 10°\text{C}$$

Use Eq. (1) to find the Kelvin temperature:

$$T = T_C + 273.15 = 10°\text{C} + 273.15 = 283\ \text{K}$$

Macroscopic Description of an Ideal Gas

The **volume expansion equation** $\Delta V = \beta V_i \, \Delta T$ is based on the assumption that the material has an **initial volume** V_i before the temperature change occurs. Such is the case for solids and liquids because they have a **fixed volume** at a given temperature.

The case for gases is completely different. The **interatomic forces** within gases are **very weak**, and, in many cases, we can imagine these forces to be **nonexistent**. Therefore, there is **no equilibrium separation** for the atoms and **no "standard" volume** at a given temperature.

As a result, we cannot express changes in volume ΔV in a process on a gas with above Equation because we have no defined volume V_i at the beginning of the process, in the case of gases the volume **depends** on the size of the container. Equations involving gases contain the volume V, rather than a *change* in the volume from an initial value, as a variable.

Macroscopic Description of an Ideal Gas

For a gas, it is useful to know how the quantities volume *V*, pressure *P*, and temperature *T* are **related** for a sample of gas of mass *m*. In general, the equation that interrelates these quantities, called the ***equation of state***, is very complicated. If the gas is **maintained** at a very low pressure (or low density), however, the equation of state is quite simple and can be determined from experimental results. Such a low-density gas is commonly referred to as an **ideal gas**.

It is convenient to express the amount of gas in a given volume in terms of the **number of moles *n***. One mole of any substance is that amount of the substance that contains **Avogadro's number** $N_A = 6.022 \times 10^{23}$ of constituent particles (atoms or molecules). The number of moles *n* of a substance is **related** to its mass *m* through the expression:

$$n = \frac{m}{M}$$

where *M* is the **molar mass** of the substance. The **molar mass** of each chemical element is the **atomic mass** expressed in *grams per mole*.

Macroscopic Description of an Ideal Gas

Now suppose an ideal gas is confined to a cylindrical container whose volume can be varied by means of a movable piston as in Figure (4). If we assume the cylinder does not leak, the **mass** (or the **number of moles**) of the gas **remains constant**.

For such a system, experiments provide the following information:

First, When the gas is kept at a constant temperature, its pressure is **inversely proportional** to the volume. (Boyle's law)

Second, When the pressure of the gas is kept constant, the volume is **directly proportional** to the temperature. (Charles's law)

Third, When the volume of the gas is kept constant, the pressure is **directly proportional** to the temperature. (Gay–Lussac's law)

Figure (4): An ideal gas confined to a cylinder whose volume can be varied by means of a movable piston.

Macroscopic Description of an Ideal Gas

These observations are summarized by the **equation of state** for an *ideal gas*:

$$\boxed{PV = nRT} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ (4)$$

In this expression, also known as the **ideal gas law**, n is the number of moles of gas in the sample and R is a constant. Experiments on numerous gases show that as the pressure approaches zero, the quantity PV/nT approaches the same value R for all gases. For this reason, R is called the **universal gas constant**.

In SI units, in which pressure is expressed in ***pascals*** (1 Pa = 1 N/m^2) and volume in ***cubic meters***, the product PV has units of ***newton . meters***, or joules, and R has the value:

$$R = 8.314\ \mathrm{J/mol \cdot K}$$

The **ideal gas law** states that if the *volume* and *temperature* of a fixed amount of gas do not change, the *pressure* also remains constant.

Macroscopic Description of an Ideal Gas

The **ideal gas law** is often expressed in terms of the total number of molecules *N*. Because the **number of moles *n*** equals the ratio of the total number of molecules *N* and Avogadro's number N_A, we can write Equation (4) as:

$$PV = nRT = \frac{N}{N_A}RT$$

$$PV = Nk_BT$$

where k_B is **Boltzmann's constant**, which has the value:

$$k_B = \frac{R}{N_A} = 1.38 \times 10^{-23}\,\mathrm{J/K}$$

It is common to call quantities such as *P*, *V*, and *T* the **thermodynamic variables** of an ideal gas. If the equation of state is known, one of the variables can always be expressed as some function of the other two.

Macroscopic Description of an Ideal Gas

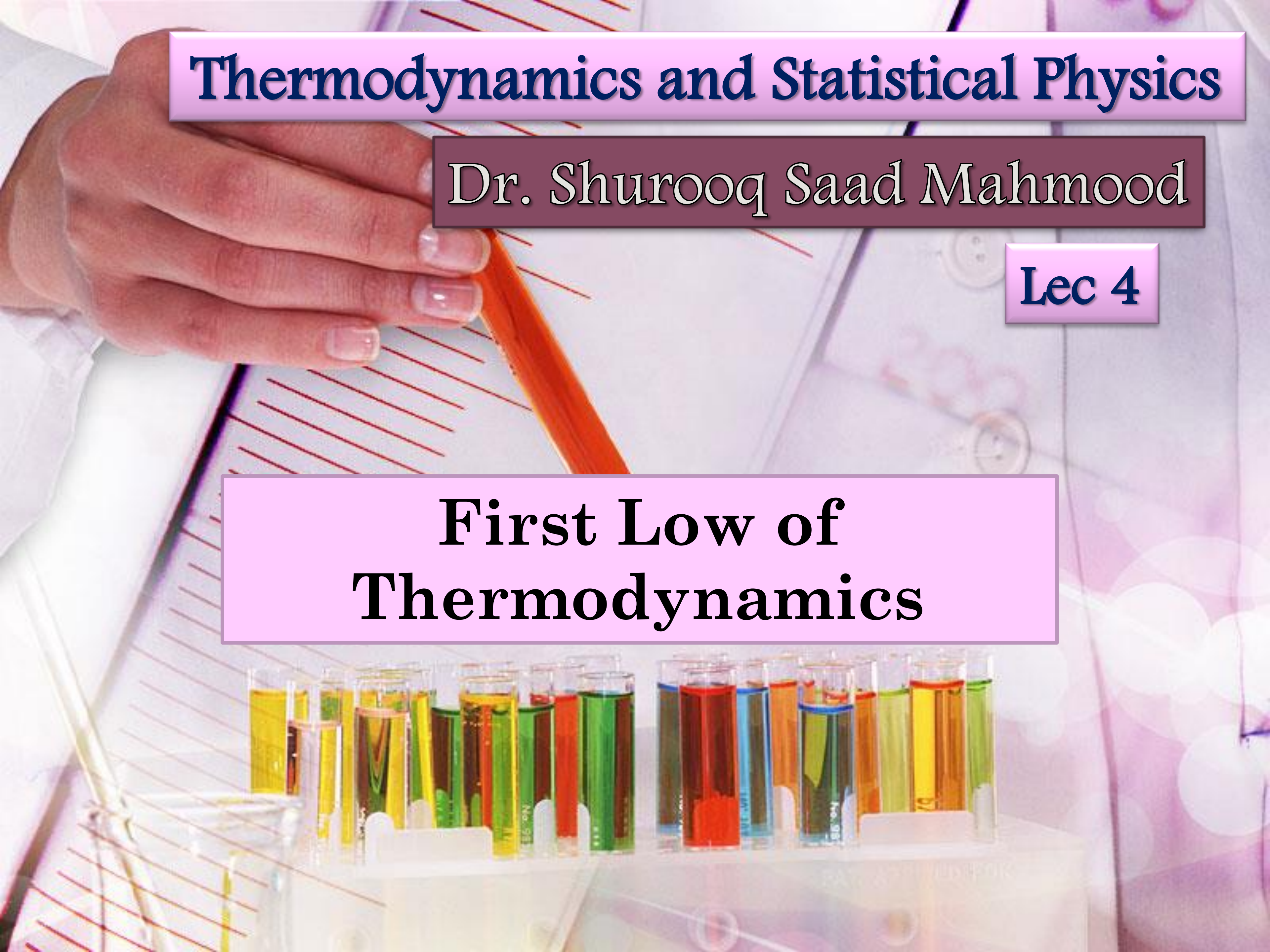
Example 2: How Many Moles of Gas in a Container

An ideal gas occupies a volume of 100 cm^3 at 20 °C and 100 Pa. Find the number of moles of gas in the Container.

Solution

$$n = \frac{PV}{RT} = \frac{(100\ \text{Pa})(1.00 \times 10^{-4}\ \text{m}^3)}{(8.314\ \text{J/mol}\cdot\text{K})(293\ \text{K})}$$

$$= 4.11 \times 10^{-6}\ \text{mol}$$

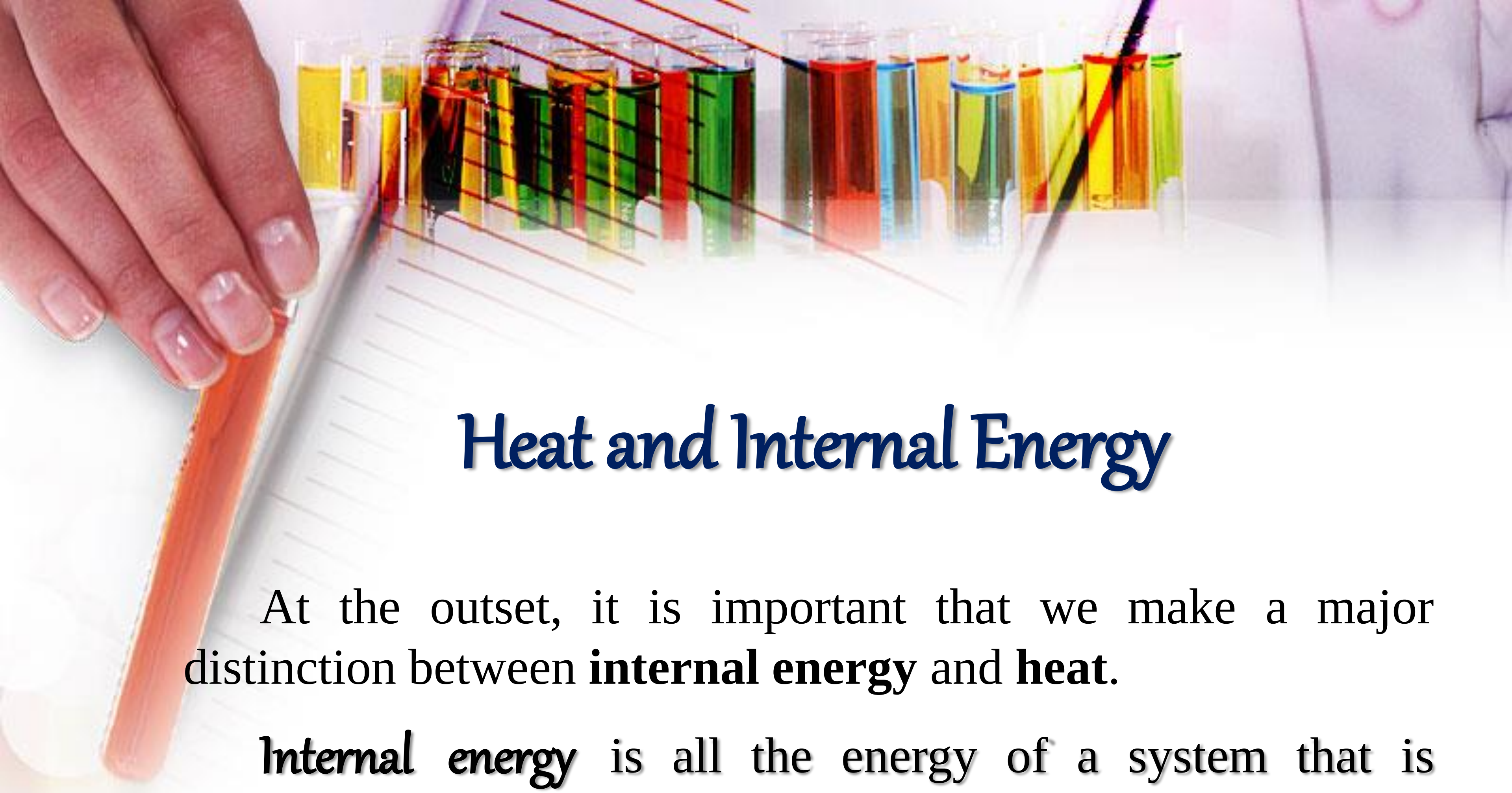


Thermodynamics and Statistical Physics

Dr. Shurooq Saad Mahmood

Lec 4

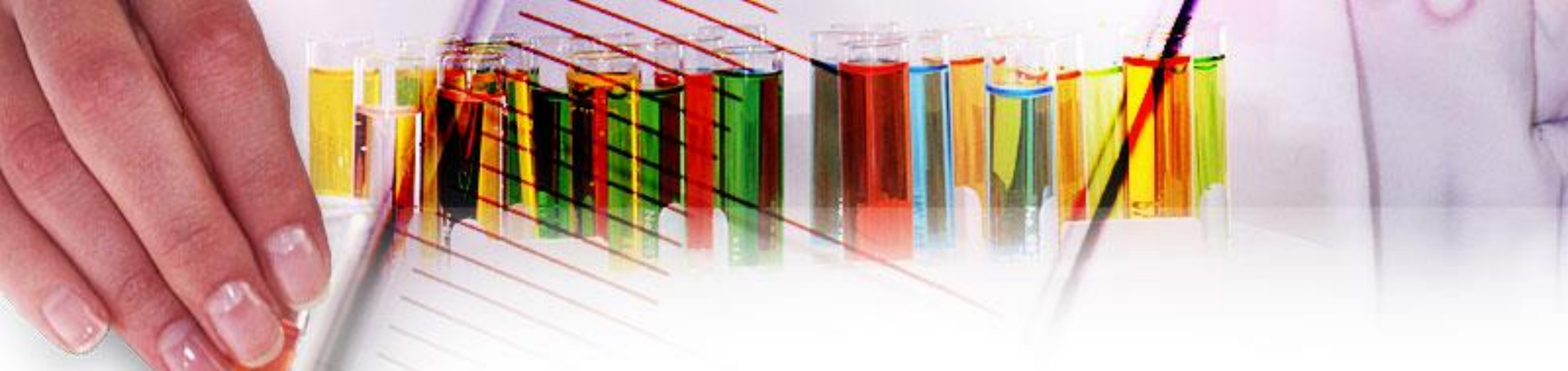
First Low of Thermodynamics



Heat and Internal Energy

At the outset, it is important that we make a major distinction between **internal energy** and **heat**.

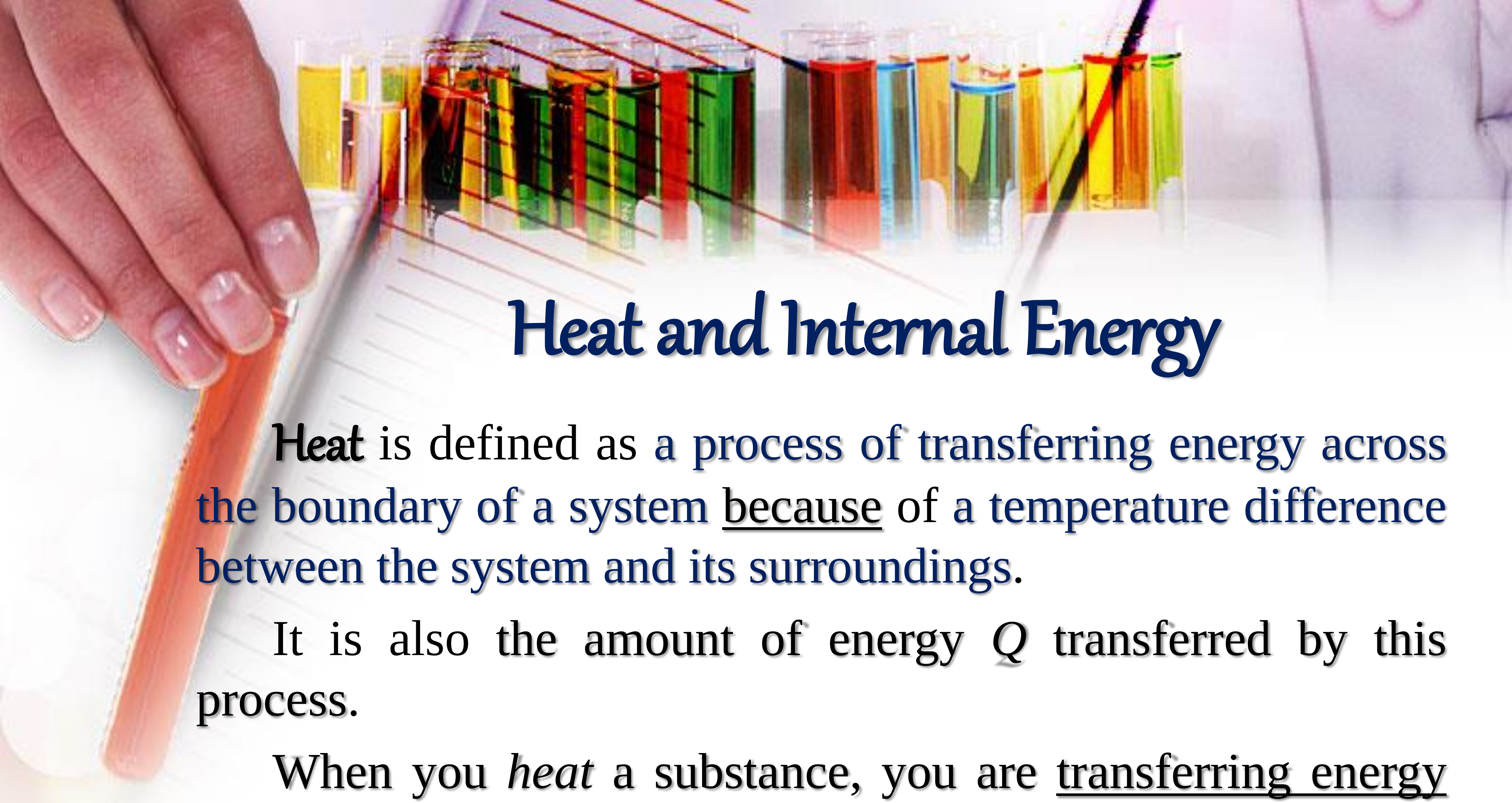
Internal energy is all the energy of a system that is associated with its microscopic components -*atoms* and *molecules*- when viewed from a reference frame at rest with respect to the center of mass of the system.



Heat and Internal Energy

Internal energy includes (1) kinetic energy of random translational, rotational, and vibrational motion of molecules; (2) vibrational potential energy associated with forces between atoms in molecules; and (3) electric potential energy associated with forces between molecules.

It is useful to relate **internal energy** to the **temperature** of an object, but this relationship is limited. Internal energy changes can also occur in the absence of temperature changes.



Heat and Internal Energy

Heat is defined as a process of transferring energy across the boundary of a system because of a temperature difference between the system and its surroundings.

It is also the amount of energy Q transferred by this process.

When you *heat* a substance, you are transferring energy into it by placing it in **contact** with surroundings that have a *higher temperature*. Such is the case, for example, when you place a pan of cold water on a stove burner. The burner is at a *higher temperature* than the *water*, and so the water **gains** energy by **heat**.

Remarks

1) internal energy = thermal energy + bond energy

2) **Thermal energy** can be interpreted as that part of the internal energy associated with **random motion of molecules** and, therefore, related **to temperature**.

3) **Bond energy** is the intermolecular potential energy.

The difference between heat and internal energy

1) One can refer to ***heat*** only when energy has been transferred as a result of a **temperature difference**. Both heat and work are ways of changing the energy of a system.

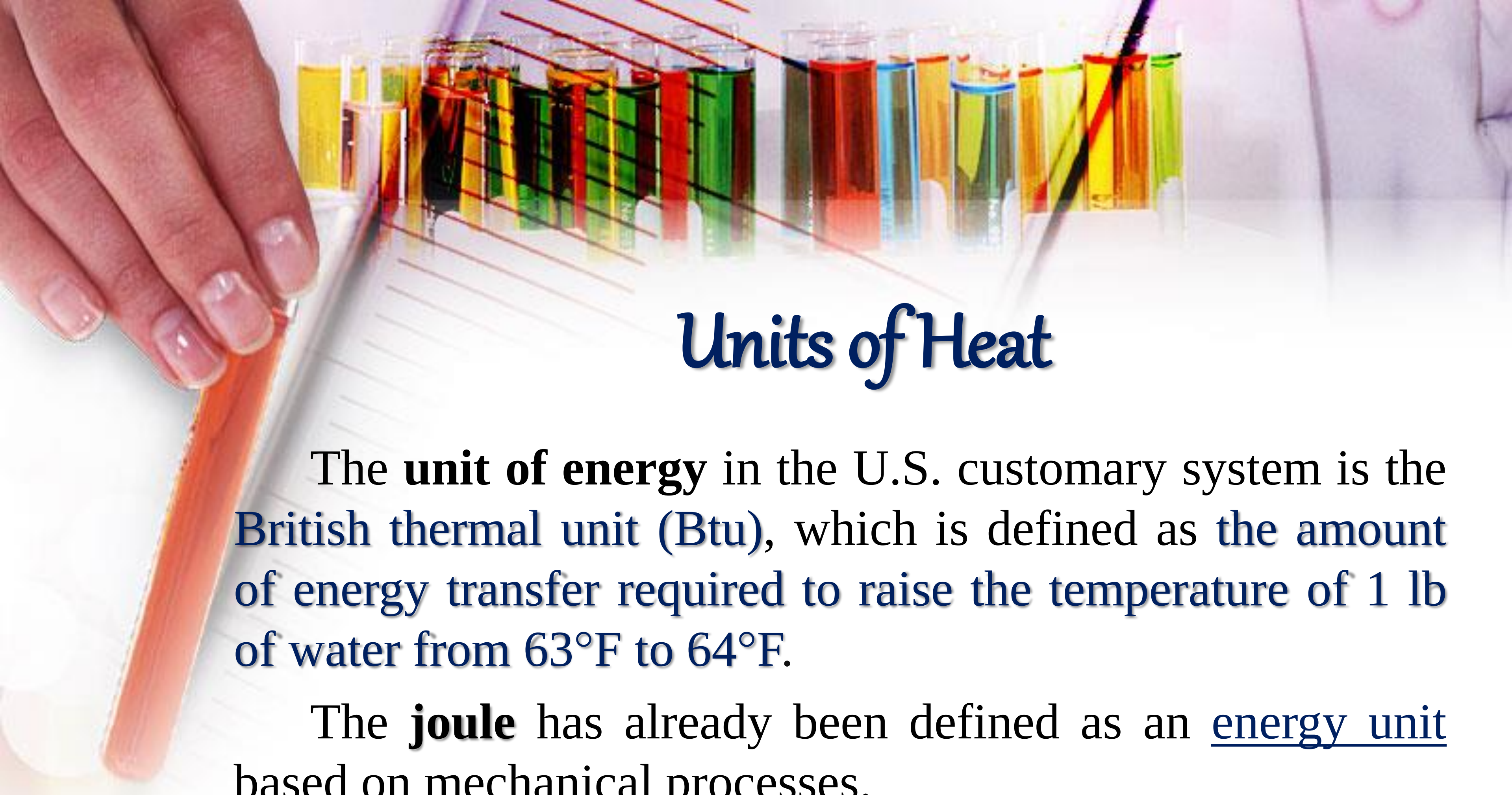
2) the internal energy of a system can be changed even when no energy is transferred by heat.

For example, when a gas in an insulated container is compressed by a piston, the temperature of the gas and its internal energy increase, but no transfer of energy by heat from the surroundings to the gas has occurred.

Units of Heat

Early studies of heat focused on the resultant increase in temperature of a substance, which was often *water*. Initial notions of heat were based on a fluid called *caloric* that flowed from one substance to another and caused changes in temperature.

From the name of this mythical fluid came an **energy unit** related to thermal processes, the **calorie** (**cal**), which is defined as the amount of energy transfer necessary to raise the temperature of 1 g of water from 14.5°C to 15.5°C.



Units of Heat

The **unit of energy** in the U.S. customary system is the British thermal unit (Btu), which is defined as the amount of energy transfer required to raise the temperature of 1 lb of water from 63°F to 64°F.

The **joule** has already been defined as an energy unit based on mechanical processes.

Scientists are increasingly turning away from the *calorie* and the *Btu* and are using the **joule** when describing thermal processes.

the SI *unit of energy, the* ***joule***.

The Mechanical Equivalent of Heat

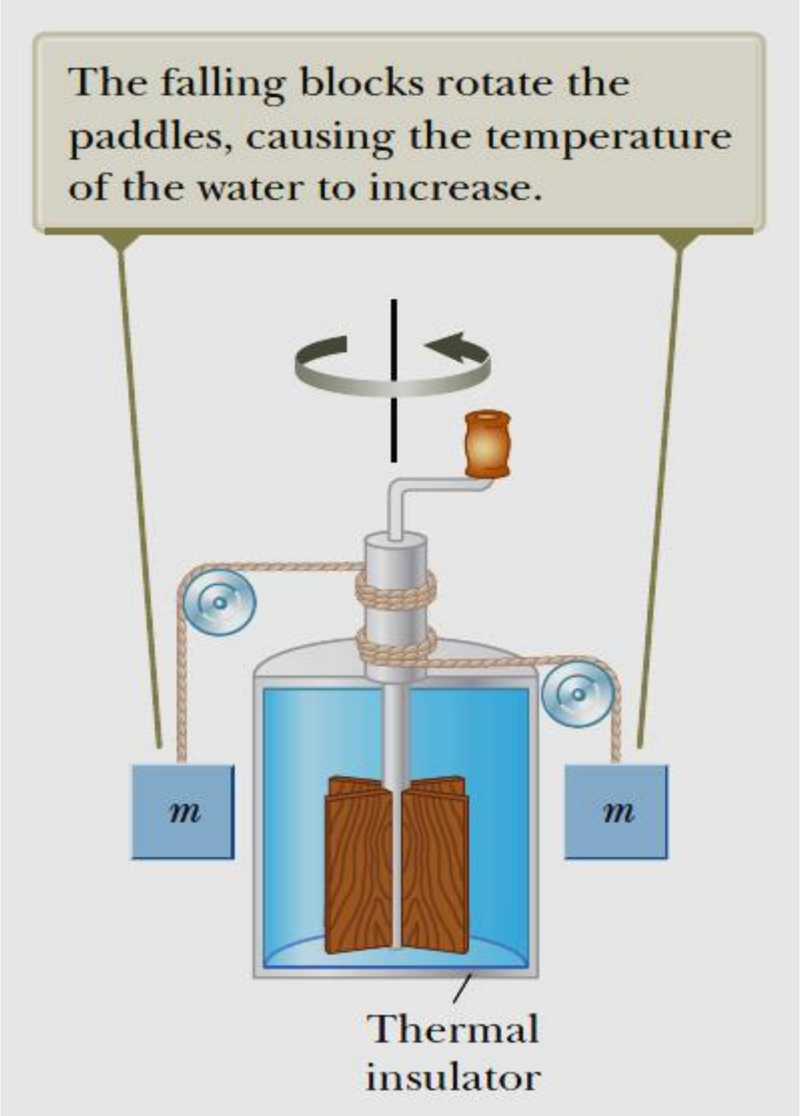
Mechanical energy is not conserved in the presence of nonconservative forces. Various experiments show that this lost mechanical energy does not simply disappear but **is transformed into internal energy**. We can perform such an experiment at home by simply hammering a nail into a scrap piece of wood.

What happens to all the kinetic energy of the hammer once we have finished? Some of it is now in the nail as internal energy, as demonstrated by the fact that the nail is measurably warmer. Although this connection between mechanical and internal energy was first suggested by *Benjamin Thompson*, it was *Joule* who established the **equivalence of these two forms of energy**.

The Mechanical Equivalent of Heat

A schematic diagram of Joule’s most famous experiment is shown in Figure 1. The system of interest is the water in a thermally insulated container. Work is done on the *water* by a rotating paddle wheel, which is driven by heavy blocks falling at a constant speed. The stirred water is warmed due to the friction between it and the paddles. If the *energy lost* in the bearings and through the walls is neglected, then the loss in potential energy associated with the blocks **equals** the work done by the paddle wheel on the water.

The Mechanical Equivalent of Heat



The falling blocks rotate the paddles, causing the temperature of the water to increase.

Figure 1: Joule’s experiment for determining the mechanical equivalent of heat.

The Mechanical Equivalent of Heat

If the two blocks fall through a distance h, the loss in potential energy is $2mgh$, where m is the mass of one block; it is this energy that causes the temperature of the water to increase. By varying the conditions of the experiment, Joule found that the loss in mechanical energy $2mgh$ is proportional to the increase in water temperature ΔT.

The proportionality constant was found to be approximately **4.18 J/g .°C**.

Hence, 4.18 J of mechanical energy raises the temperature of 1 g of water by 1°C.

The Mechanical Equivalent of Heat

More precise measurements taken later demonstrated the proportionality to be **4.186 J/g .°C** when the temperature of the water was raised from 14.5°C to 15.5°C.

$$1 \text{ cal} \equiv 4.186 \text{ J}$$

This equality is known, for purely historical reasons, as the **mechanical equivalent of heat**.

Thermodynamics and Statistical Physics

Dr. Shurooq Saad Mahmood

Lec 5

First Low of Thermodynamics

The Mechanical Equivalent of Heat

Example 1: **Losing Weight the Hard Way**

A student eats a dinner rated at 2000 Calories. He wishes to do an equivalent amount of work in the gymnasium by lifting a 50.0 kg barbell. How many times must he raise the barbell to expend this much energy? Assume he raises the barbell 2.00 m each time he lifts it and he regains no energy when he lowers the barbell.

Solution

Conceptualize: Imagine the student raising the barbell. He is doing work on the system of the barbell and the Earth, so energy is leaving his body. The total amount of work that the student must do is 2000 Calories.

The conservation of energy equation

$$(1) \quad \Delta U_{\text{total}} = W_{\text{total}}$$

The Mechanical Equivalent of Heat

Express the **change in gravitational potential energy** of the system after the barbell is raised once:

$$\Delta U = mgh$$

Express the total amount of energy that must be transferred into the system by work for lifting the barbell *n* times, assuming energy is not regained when the barbell is lowered:

$$(2) \quad \Delta U_{\text{total}} = nmgh$$

Substitute Equation (2) into Equation (1):

$$nmgh = W_{\text{total}}$$

The Mechanical Equivalent of Heat

Solve for n:

$$n = \frac{W_{\text{total}}}{mgh}$$

$$= \frac{(2\,000 \text{ Cal})}{(50.0 \text{ kg})(9.80 \text{ m/s}^2)(2.00 \text{ m})}\left(\frac{1.00 \times 10^3 \text{ cal}}{\text{Calorie}}\right)\left(\frac{4.186 \text{ J}}{1 \text{ cal}}\right)$$

$$= \boxed{8.54 \times 10^3 \text{ times}}$$

Specific Heat and Calorimetry

When **energy** is added to a **system** and there is no change in the kinetic or potential energy of the system, the **temperature** of the system usually rises. (An exception to this statement is the case in which a system undergoes a **change of state**—also called a **phase transition**—).

If the system consists of a sample of a substance, we find that the quantity of energy required to raise the temperature of a given mass of the substance by some amount varies from one substance to another. For example, the quantity of energy required to raise the temperature of 1 kg of water by 1°C is 4 186 J, but the quantity of energy required to raise the temperature of 1 kg of copper by 1°C is only 387 J.

Specific Heat and Calorimetry

The **heat capacity *C*** of a particular sample is defined as the amount of energy needed to raise the temperature of that sample by 1°C. From this definition, we see that if **energy *Q*** produces a **change *ΔT* in the temperature of a sample**, then

$$Q = C\Delta T$$

The **specific heat c** of a substance is the heat capacity per unit mass. Therefore, if **energy *Q*** transfers to **a sample of a substance with mass *m*** and the **temperature of the sample changes by *ΔT***, the **specific heat** of the substance is:

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

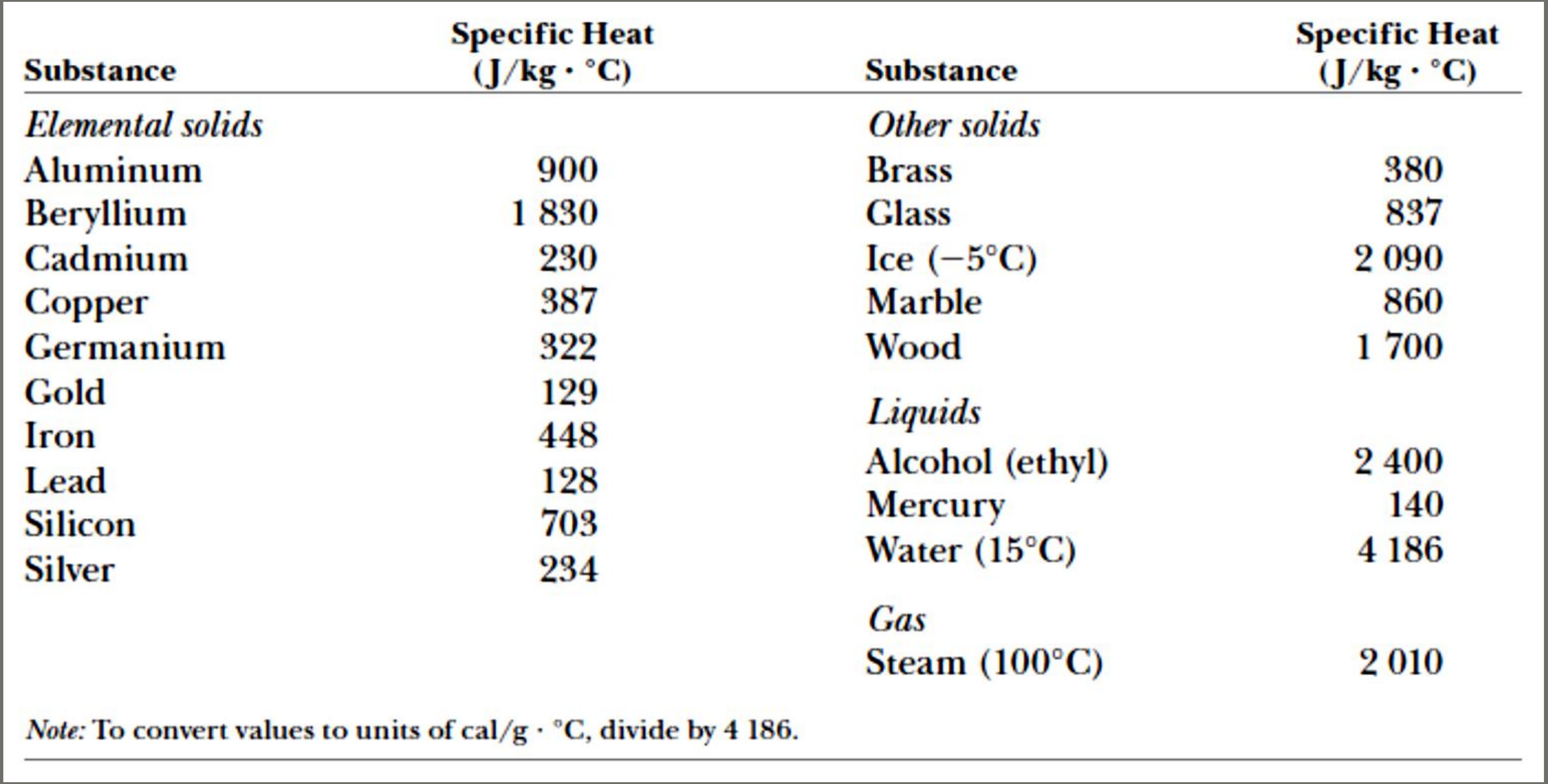
Specific Heat and Calorimetry

Specific heat is essentially a measure of how thermally insensitive a substance is to the addition of energy. The greater a material's specific heat, the more energy must be added to a given mass of the material to **cause** a particular temperature change. Table (1) lists representative specific heats.

From this definition, we can **relate the energy Q transferred** between a sample of mass m of a material and its surroundings **to a temperature change ΔT** as:

$$Q = mc\,\Delta T \qquad \text{............(1)}$$

Table 1: Specific Heats of Some Substances at 25°C and Atmospheric Pressure



Substance	**Specific Heat (J/kg · °C)**	**Substance**	**Specific Heat (J/kg · °C)**
Elemental solids		*Other solids*	
Aluminum	900	Brass	380
Beryllium	1 830	Glass	837
Cadmium	230	Ice (−5°C)	2 090
Copper	387	Marble	860
Germanium	322	Wood	1 700
Gold	129	*Liquids*	
Iron	448	Alcohol (ethyl)	2 400
Lead	128	Mercury	140
Silicon	703	Water (15°C)	4 186
Silver	234	*Gas*	
		Steam (100°C)	2 010

Note: To convert values to units of cal/g · °C, divide by 4 186.

Specific Heat and Calorimetry

For example, the **energy required** to raise the **temperature** of 0.500 kg of water by 3.00°C is:

$$\boldsymbol{Q = (0.500\ \text{kg})(4\,186\ \text{J/kg}\ .\ ^\circ\text{C})(3.00^\circ\text{C}) = 6.28 \times 10^3\ \text{J}.}$$

Notice that when the temperature increases, Q and ΔT are taken to be positive and energy transfers into the system. When the temperature decreases, Q and ΔT are negative and energy transfers out of the system.

Specific heat varies with temperature

Specific heat varies with temperature. If, however, temperature intervals are not too great, the temperature variation can be ignored and c can be treated as a **constant**. For example, the specific heat of water varies by only about 1% from 0°C to 100°C at atmospheric pressure.

Calorimetry

One **technique for measuring specific heat** involves heating a sample to some known temperature *Tx*, **placing it** in a vessel containing water of known mass and temperature *Tw* < *Tx*, and **measuring** the temperature of the water **after equilibrium has been reached**.

This technique is called **calorimetry**, and devices in which this energy transfer occurs are called **calorimeters**.

Figure (1) shows the hot sample in the cold water and the **resulting** energy transfer by heat from the high-temperature part of the system to the low-temperature part.

If the **system** of the sample and the water is **isolated**, the principle of conservation of energy **requires** that **the amount of energy Q_{hot} that leaves the sample** (of unknown specific heat) **equal the amount of energy Q_{cold} that enters the water**.

Calorimetry

Conservation of energy allows us to write the mathematical representation of this energy statement as:

$$Q_{\text{cold}} = -Q_{\text{hot}} \qquad \text{...........(2)}$$

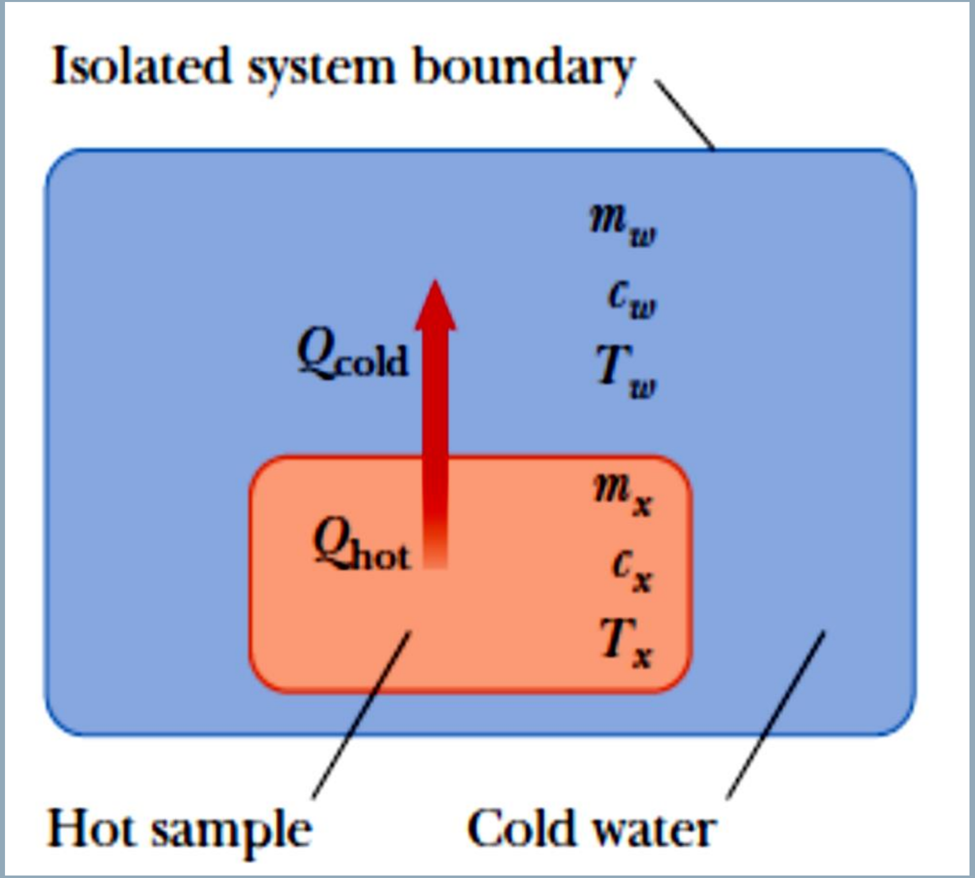


Figure 1: In a calorimetry experiment, a hot sample whose specific heat is unknown is placed in cold water in a container that isolates the system from the environment.

Calorimetry

Suppose **m_x is the mass** of a sample of some substance whose specific heat we wish to determine. Let's call its **specific heat c_x** and its **initial temperature T_x** as shown in Figure (1).

Likewise, let **m_w**, **c_w**, and **T_w** represent corresponding values for the water. If **T_f** is the **final temperature** after the system comes to equilibrium,

Equation (1) shows that the energy transfer for the water is $m_w c_w(T_f - T_w)$, which is **positive** because $T_f > T_w$, and that the energy transfer for the sample of unknown specific heat is $m_x c_x(T_f - T_x)$, which is **negative**.

Substituting these expressions into Equation (2) gives:

$$m_w c_w(T_f - T_w) = -m_x c_x(T_f - T_x)$$

This equation can be solved for the unknown **specific heat c_x**.

Calorimetry

Example 2: Cooling a Hot Ingot

A 0.050 kg ingot of metal is heated to 200.0°C and then dropped into a calorimeter containing 0.400 kg of water initially at 20.0°C. The final equilibrium temperature of the mixed system is 22.4°C. Find the specific heat of the metal.

Solution

$$m_w c_w (T_f - T_w) = -m_x c_x (T_f - T_x)$$

Solve for c_x:

$$c_x = \frac{m_w c_w (T_f - T_w)}{m_x (T_x - T_f)}$$

Calorimetry

Example 2: Cooling a Hot Ingot

A 0.050 kg ingot of metal is heated to 200.0°C and then dropped into a calorimeter containing 0.400 kg of water initially at 20.0°C. The final equilibrium temperature of the mixed system is 22.4°C. Find the specific heat of the metal.

Solution

Substitute numerical values:

$$c_x = \frac{(0.400\ \text{kg})(4\,186\ \text{J/kg}\cdot{}^\circ\text{C})(22.4^\circ\text{C} - 20.0^\circ\text{C})}{(0.050\,0\ \text{kg})(200.0^\circ\text{C} - 22.4^\circ\text{C})}$$

$$= \boxed{453\ \text{J/kg}\cdot{}^\circ\text{C}}$$

Thermodynamics and Statistical Physics

Dr. Shurooq Saad Mahmood

Lec 6

First Low of Thermodynamics

Phase Change

A substance can undergo a change in temperature when energy is transferred between it and its surroundings. In some situations, however, the transfer of energy does not result in a change in temperature.

That is the case whenever **the physical characteristics of the substance change from one form to another**; such a change is commonly referred to as a **phase change**.

- Two common phase changes are
  - **Solid to liquid (melting)**
  - **Liquid to gas (boiling)**

All such phase changes involve a change in the system’s internal energy but no change in its temperature.

Phase Change

The increase in internal energy in boiling, for example, is represented by the breaking of bonds between molecules in the liquid state; this bond breaking allows the molecules to move farther apart in the gaseous state, with a corresponding increase in intermolecular potential energy.

Different substances respond differently to the addition or removal of energy as they change phase because their internal molecular arrangements vary. Also, the amount of energy transferred during a phase change depends on the amount of substance involved. (It takes less energy to melt an ice cube than it does to thaw a frozen lake).

Phase Change

When discussing two phases of a material, we will use the term *higher-phase material* to mean the material existing at the higher temperature.

So, for example, if we discuss water and ice, water is the higher-phase material, whereas steam is the higher-phase material in a discussion of steam and water.

Latent Heat

Consider a system containing a substance in two phases in equilibrium such as water and ice. The initial amount of the higher-phase material, **water**, in the system is $\boldsymbol{m_i}$. Now imagine that **energy $\boldsymbol{Q}$ enters the system**. As a result, the final amount of water is $\boldsymbol{m_f}$ due to the melting of some of the ice. Therefore, the amount of ice that melted, equal to the amount of *new* water, is $\Delta m = m_f - m_i$. We define the **latent heat** for this phase change as

$$L \equiv \frac{Q}{\Delta m}$$

This parameter is called **latent heat** (literally, the **"hidden" heat**) because this added or removed energy does not result in a temperature change. The **value of $\boldsymbol{L}$** for a substance depends on the nature of the phase change as well as on the properties of the substance.

Latent Heat

Latent heat, energy absorbed or released by a substance during a change in its physical state (phase) that occurs without changing its temperature.

From the definition of latent heat, and again choosing heat as our energy transfer mechanism, the **energy required to change the phase** of a pure substance is

$$Q = L\,\Delta m$$

Energy transferred to a substance during a phase change

where Δm is the change in mass of the *higher-phase material*.

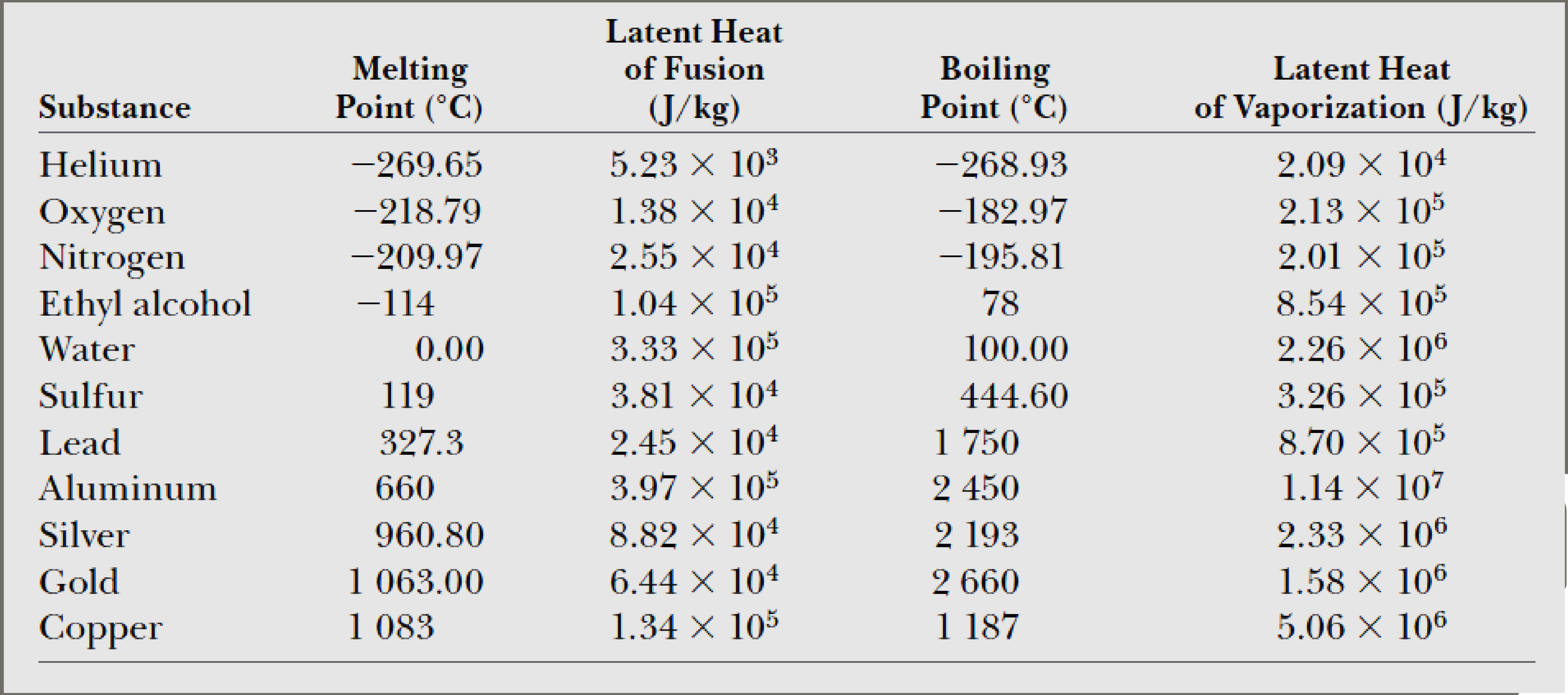
Latent Heat

Latent heat of fusion L_f is the term used when the phase change is from solid to liquid (to fuse means “to combine by melting”), the latent heat associated with melting a solid or freezing a liquid is called the heat of fusion.

And latent heat of vaporization L_v is the term used when the phase change is from liquid to gas (the liquid “vaporizes”), the latent heat associated with vaporizing a liquid or a solid or condensing a vapour is called the heat of vaporization.

The latent heats of various substances vary considerably as data in Table 2 show.

Table 2: Latent Heats of Fusion and Vaporization



Substance	Melting Point (°C)	Latent Heat of Fusion (J/kg)	Boiling Point (°C)	Latent Heat of Vaporization (J/kg)
Helium	−269.65	5.23×10^3	−268.93	2.09×10^4
Oxygen	−218.79	1.38×10^4	−182.97	2.13×10^5
Nitrogen	−209.97	2.55×10^4	−195.81	2.01×10^5
Ethyl alcohol	−114	1.04×10^5	78	8.54×10^5
Water	0.00	3.33×10^5	100.00	2.26×10^6
Sulfur	119	3.81×10^4	444.60	3.26×10^5
Lead	327.3	2.45×10^4	1 750	8.70×10^5
Aluminum	660	3.97×10^5	2 450	1.14×10^7
Silver	960.80	8.82×10^4	2 193	2.33×10^6
Gold	1 063.00	6.44×10^4	2 660	1.58×10^6
Copper	1 083	1.34×10^5	1 187	5.06×10^6

Latent Heat

To understand the role of latent heat in phase changes, consider the energy required to convert a 1.00g cube of ice at −30.0°C to steam at 120.0°C.

Figure (1) indicates the experimental results obtained when energy is gradually added to the ice. The results are presented as a graph of temperature of the system of the ice cube versus energy added to the system. Let's examine each portion of the red-brown curve, which is divided into parts A through E.

Latent Heat

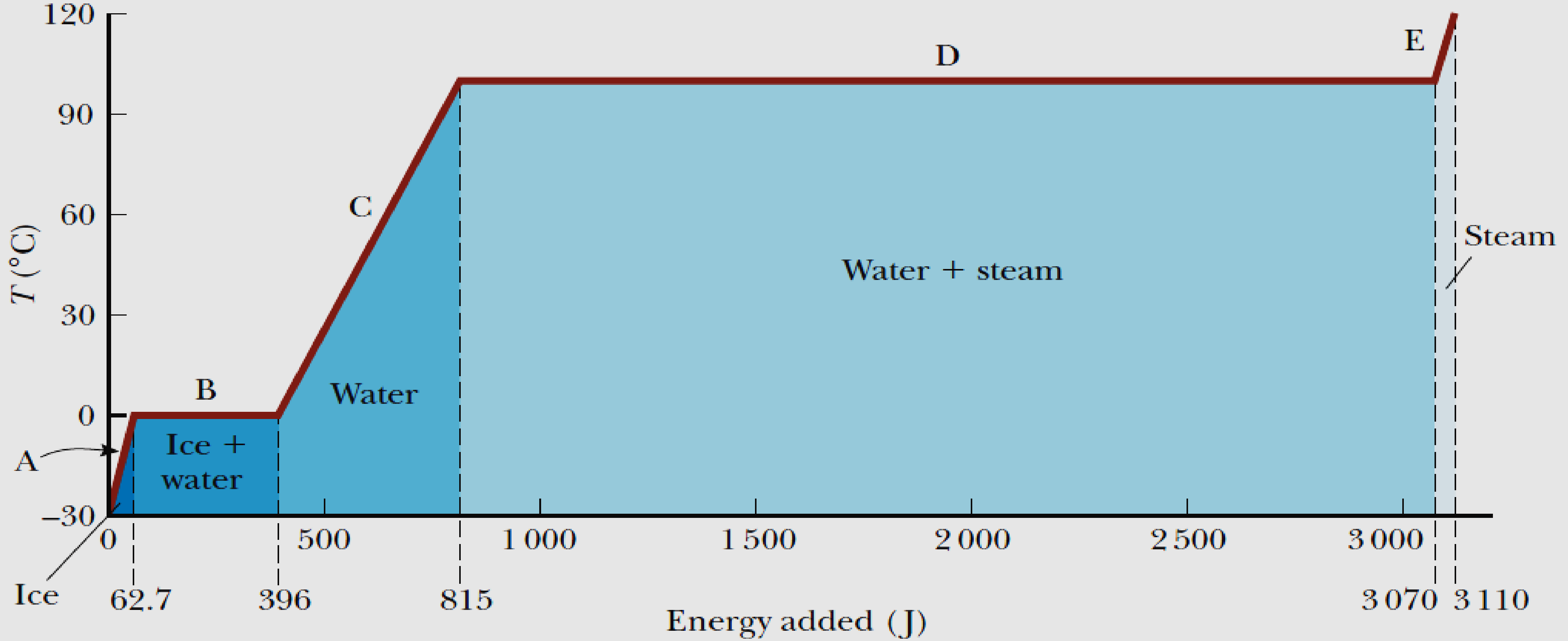


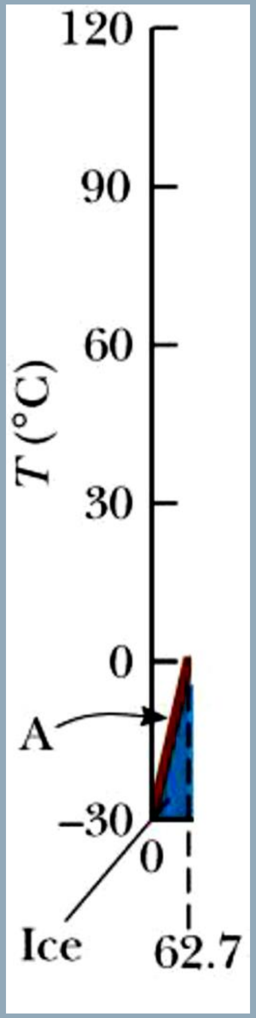
Figure 1: A plot of temperature versus energy added when 1.00 g of ice initially at −30.0°C is converted to steam at 120.0°C.

Latent Heat

Part A. On this portion of the curve, the temperature of the ice changes from −30.0°C to 0.0°C. Equation below indicates that the temperature varies linearly with the energy added, so the experimental result is a straight line on the graph. Because the **specific heat** of ice is 2 090 J/kg . °C, we can calculate **the amount of energy added** by using Equation:

$$Q = mc\,\Delta T$$

$$Q = m_i c_i\,\Delta T = (1.00 \times 10^{-3}\ \text{kg})(2\,090\ \text{J/kg}\cdot{}^\circ\text{C})(30.0^\circ\text{C}) = 62.7\ \text{J}$$



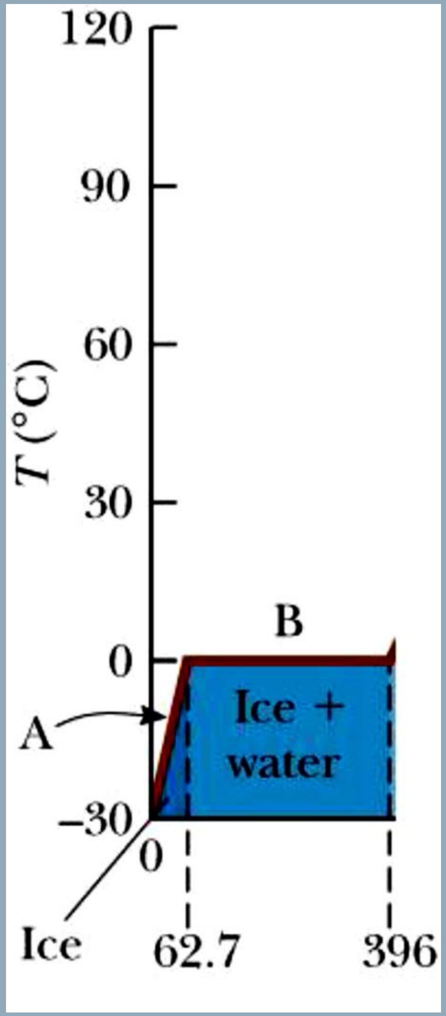
Latent Heat

Part B. When the temperature of the ice reaches 0.0°C, the ice–water mixture remains at this temperature —even though energy is being added— until all the ice melts. The **energy required to melt 1.00 g of ice at 0.0°C is**, from Equation:

$$Q = L\,\Delta m$$

$$Q = L_f\,\Delta m_w = L_f m_i = (3.33 \times 10^5\,\mathrm{J/kg})(1.00 \times 10^{-3}\,\mathrm{kg}) = 333\,\mathrm{J}$$

At this point, we have moved to the 396 J (= 62.7 J + 333 J) mark on the energy axis in Figure 1.

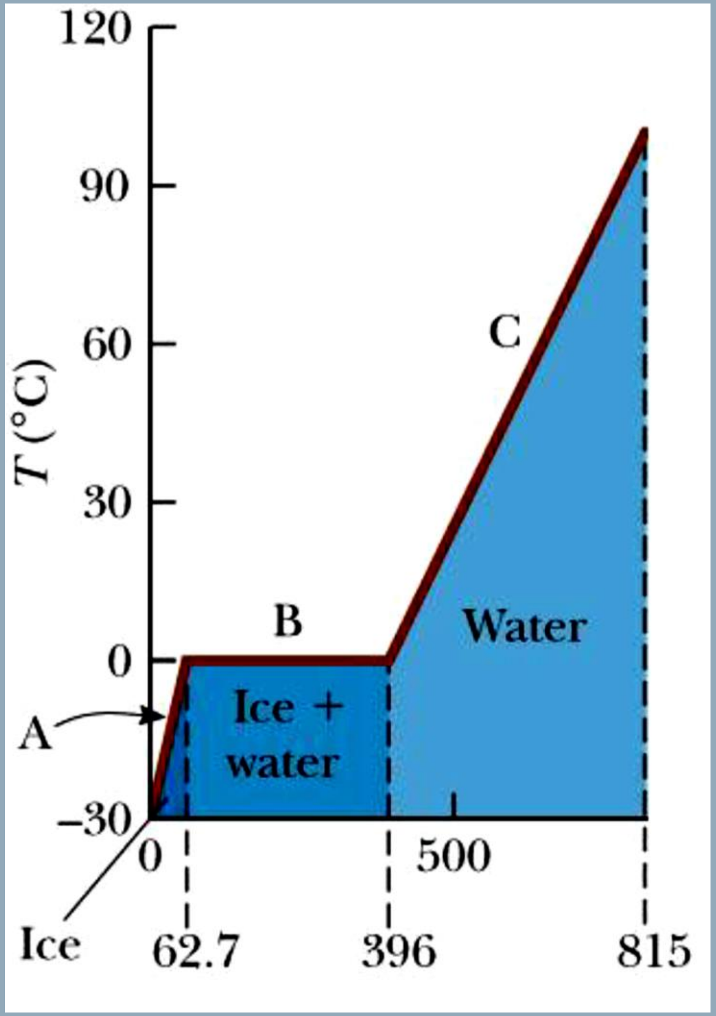


Latent Heat

Part C. Between 0.0°C and 100.0°C, nothing surprising happens. No phase change occurs, and so all energy added to the water is used to increase its temperature. **The amount of energy necessary to increase the temperature from 0.0°C to 100.0°C is**

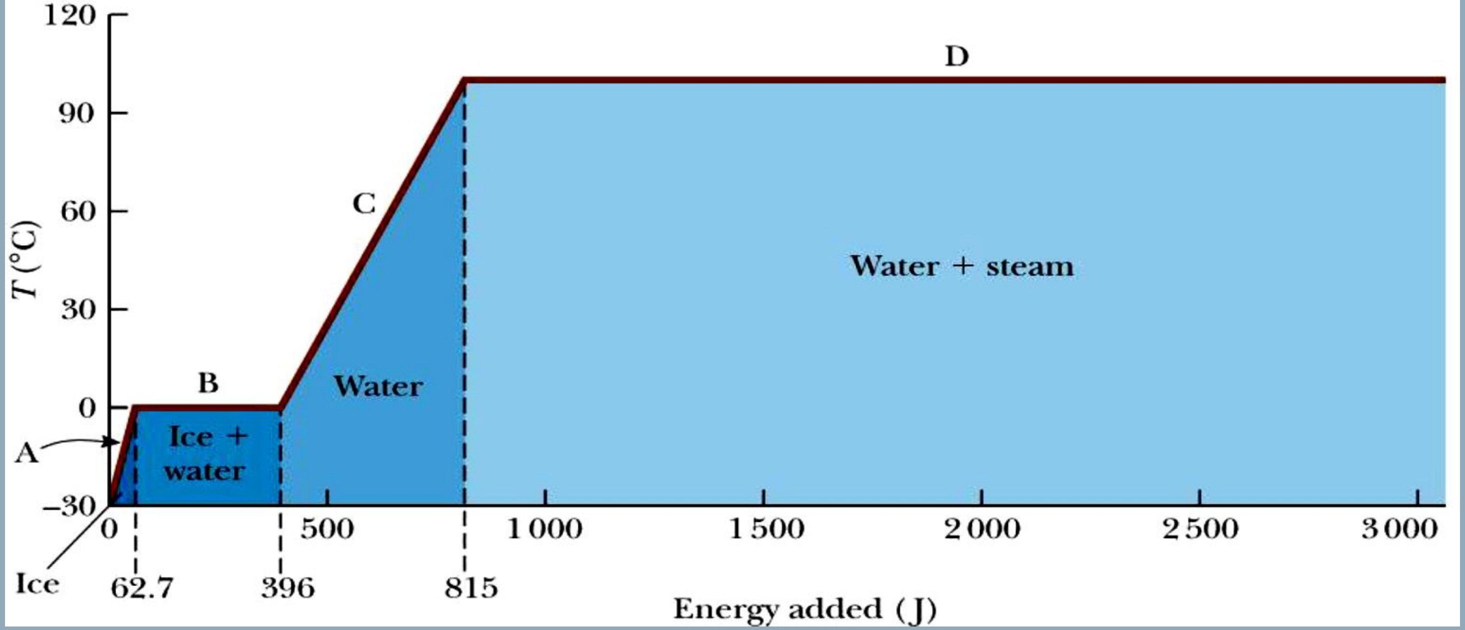
$$Q = m_w c_w \Delta T$$

$$= (1.00 \times 10^{-3}\ \text{kg})(4.19 \times 10^{3}\ \text{J/kg} \cdot {}^\circ\text{C})(100.0^\circ\text{C}) = 419\ \text{J}$$



Latent Heat

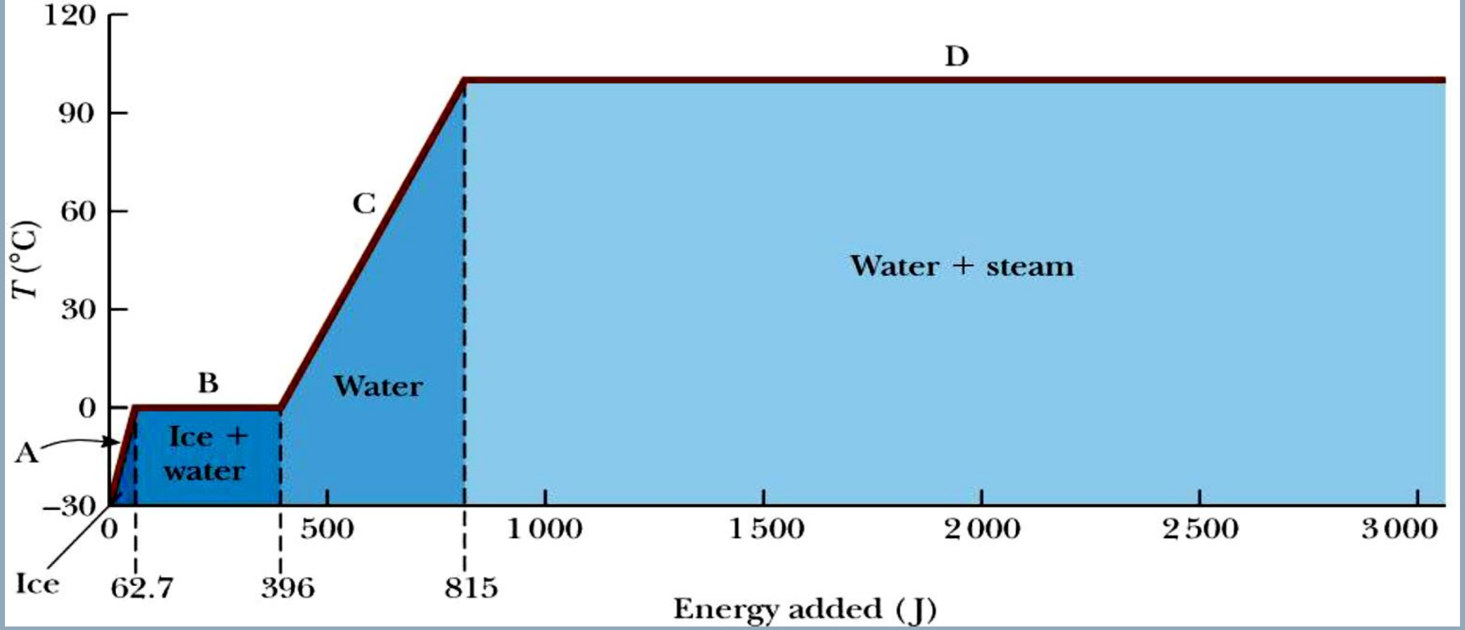
Part D. At 100.0°C, another phase change occurs as the water changes from water at 100.0°C to steam at 100.0°C. Similar to the ice–water mixture in **part B**, the water–steam mixture remains at 100.0°C—even though energy is being added— until all the liquid has been converted to steam.



Latent Heat

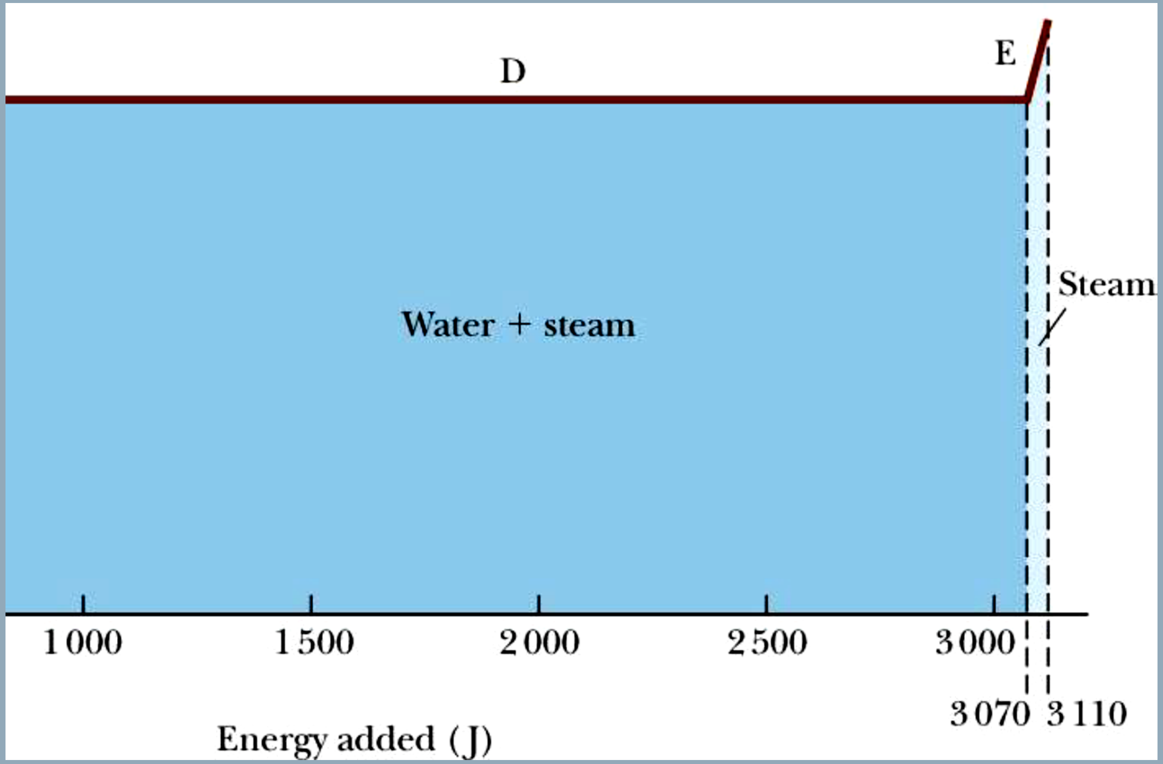
Part D. The energy required to convert 1.00 g of water to steam at 100.0°C is

$$Q = L_v \Delta m_s = L_v m_w = (2.26 \times 10^6 \text{ J/kg})(1.00 \times 10^{-3} \text{ kg}) = 2.26 \times 10^3 \text{ J}$$



Latent Heat

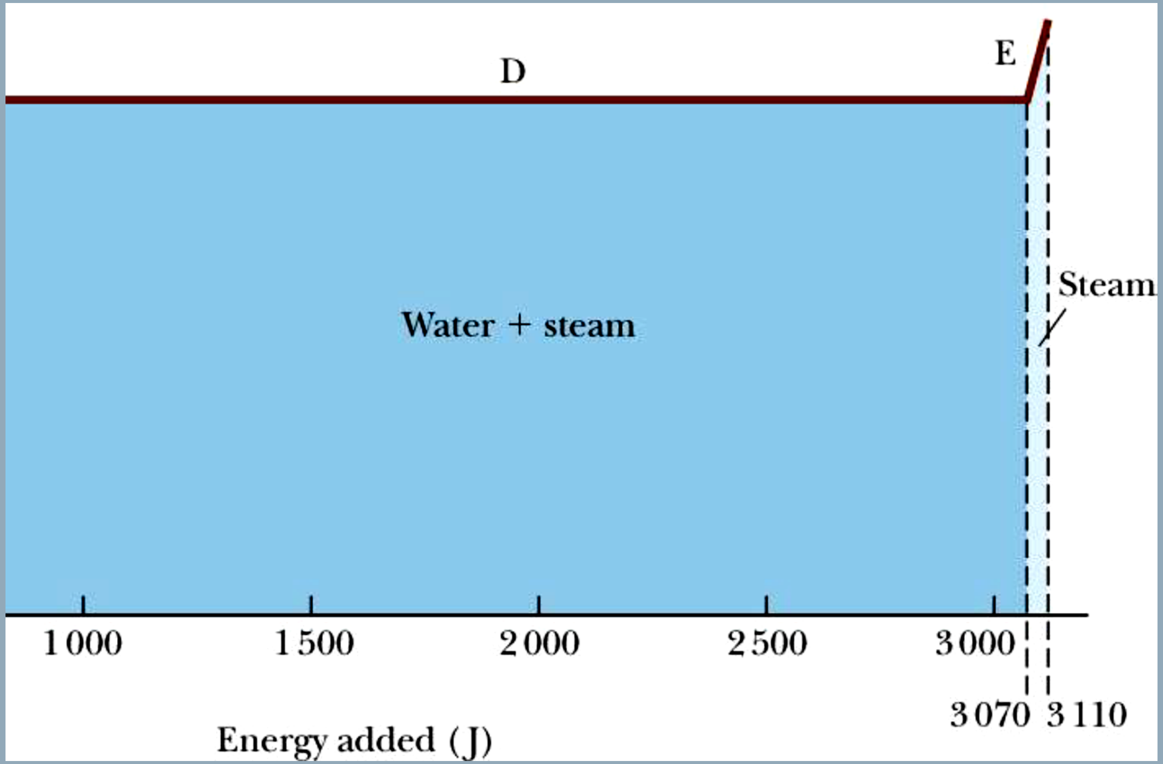
Part E. On this portion of the curve, as in **parts A and C**, no phase change occurs; therefore, all energy added is used to increase the temperature of the steam.



Latent Heat

Part E. The energy that must be added to raise the temperature of the steam from 100.0°C to 120.0°C is

$$Q = m_s c_s \Delta T = (1.00 \times 10^{-3}\ \text{kg})(2.01 \times 10^3\ \text{J/kg} \cdot {}^\circ\text{C})(20.0^\circ\text{C}) = 40.2\ \text{J}$$



Latent Heat

The total amount of energy that must be added to change 1 g of ice at −30.0°C to steam at 120.0°C is the sum of the results from all five parts of the curve, which is 3.11×10^3 J. Conversely, to cool 1 g of steam at 120.0°C to ice at −30.0°C, we must **remove** 3.11×10^3 J **of energy**.

Thermodynamics and Statistical Physics

Dr. Shurooq Saad Mahmood

Lec 7

First Low of Thermodynamics

Latent Heat

Example 1: **Cooling the Steam**

What mass of steam initially at 130°C is needed to warm 200 g of water in a 100-g glass container from 20.0°C to 50.0°C?

Solution

Conceptualize: Imagine placing water and steam together in a closed insulated container. The system eventually reaches a uniform state of water with a final temperature of 50.0°C.

Categorize: Based on our conceptualization of this situation, we categorize this example as one involving calorimetry in which a phase change occurs.

By write the equation that describe the calorimetry process:

$$(1) \quad Q_{\text{cold}} = -Q_{\text{hot}}$$

Latent Heat

Example 1: Cooling the Steam

What mass of steam initially at 130°C is needed to warm 200 g of water in a 100-g glass container from 20.0°C to 50.0°C?

Solution

The steam undergoes three processes:

First a **decrease in temperature** to 100°C, then **condensation into liquid water**, and finally a **decrease in temperature of the water to 50.0°C**.

Find the energy transfer in the first process using the unknown mass m_s of the steam:

$$Q_1 = m_s c_s \Delta T_s$$

Find the energy transfer in the second process:

$$Q_2 = L_v \Delta m_s = L_v(0 - m_s) = -m_s L_v$$

Latent Heat

Example 1: Cooling the Steam

What mass of steam initially at 130°C is needed to warm 200 g of water in a 100-g glass container from 20.0°C to 50.0°C?

Solution

Find the energy transfer in the third process:

$$Q_3 = m_s c_w \, \Delta T_{\text{hot water}}$$

Add the energy transfers in these three stages:

$$(2) \quad Q_{\text{hot}} = Q_1 + Q_2 + Q_3 = m_s(c_s \, \Delta T_s - L_v + c_w \, \Delta T_{\text{hot water}})$$

The 20.0°C water and the glass undergo only one process, an increase in temperature to 50.0°C. Find the energy transfer in this process:

$$(3) \quad Q_{\text{cold}} = m_w c_w \, \Delta T_{\text{cold water}} + m_g c_g \, \Delta T_{\text{glass}}$$

Latent Heat

Example 1: **Cooling the Steam**

What mass of steam initially at 130°C is needed to warm 200 g of water in a 100-g glass container from 20.0°C to 50.0°C?

Solution

Substitute Equations (2) and (3) into Equation (1):

$$m_w c_w \Delta T_{\text{cold water}} + m_g c_g \Delta T_{\text{glass}} = -m_s(c_s \Delta T_s - L_v + c_w \Delta T_{\text{hot water}})$$

Solve for m_s:

$$m_s = -\frac{m_w c_w \Delta T_{\text{cold water}} + m_g c_g \Delta T_{\text{glass}}}{c_s \Delta T_s - L_v + c_w \Delta T_{\text{hot water}}}$$

$$= -\frac{(0.200\text{ kg})(4\,186\text{ J/kg}\cdot{}^\circ\text{C})(50.0^\circ\text{C} - 20.0^\circ\text{C}) + (0.100\text{ kg})(837\text{ J/kg}\cdot{}^\circ\text{C})(50.0^\circ\text{C} - 20.0^\circ\text{C})}{(2\,010\text{ J/kg}\cdot{}^\circ\text{C})(100^\circ\text{C} - 130^\circ\text{C}) - (2.26 \times 10^6\text{ J/kg}) + (4\,186\text{ J/kg}\cdot{}^\circ\text{C})(50.0^\circ\text{C} - 100^\circ\text{C})}$$

$$= 1.09 \times 10^{-2}\text{ kg} = \boxed{10.9\text{ g}}$$

Work and Heat in Thermodynamic Processes

State variables

In thermodynamics, we describe the state of a system using such variables as pressure, volume, temperature, and internal energy. As a result, these quantities belong to a category called state variables.

State variables describe the state of a system.

For mechanical systems, the state variables include kinetic energy K and potential energy U.

A state of a system can be specified only if the system is in thermal equilibrium internally.

In the case of a gas in a container, internal thermal equilibrium requires that every part of the gas be at the same pressure and temperature.

Work and Heat in Thermodynamic Processes

Transfer variables

A second category of variables in situations involving energy is transfer variables.

Transfer variables are zero unless a process occurs in which energy is transferred across the boundary of a system.

Such a variable has a nonzero value if a process occurs in which energy is transferred across the system's boundary.

The transfer variable is positive or negative, depending on **whether energy is entering or leaving the system**.

Work and Heat in Thermodynamic Processes

Transfer variables

Because a transfer of energy across the boundary represents a change in the system, transfer variables are not associated with a given state of the system, but rather with a change in the state of the system.

- Heat and work are transfer variables.

Work and Heat in Thermodynamic Processes

In the previous sections, we discussed **heat** as a transfer variable. In this section, we study another important transfer variable for thermodynamic systems, **work**.

We investigate the work done on a deformable system, a gas. Consider a gas contained in a cylinder fitted with a movable piston (Figure (2)).

At equilibrium, the gas occupies a volume V and exerts a uniform pressure P on the cylinder's walls and on the piston. If the piston has a cross-sectional area A, the force exerted by the gas on the piston is $F = PA$.

Now let's assume we push the piston inward and compress the gas quasi-statically, that is, slowly enough to allow the system to remain essentially in internal thermal equilibrium at all times.

Work and Heat in Thermodynamic Processes

As the piston is pushed downward by an external force $\vec{\mathbf{F}} = -F\hat{\mathbf{j}}$ through a displacement of $d\vec{\mathbf{r}} = dy\,\hat{\mathbf{j}}$ (Figure (2b)), the work done on the gas is:

$$dW = \vec{\mathbf{F}} \cdot d\vec{\mathbf{r}} = -F\hat{\mathbf{j}} \cdot dy\,\hat{\mathbf{j}} = -F\,dy = -PA\,dy$$

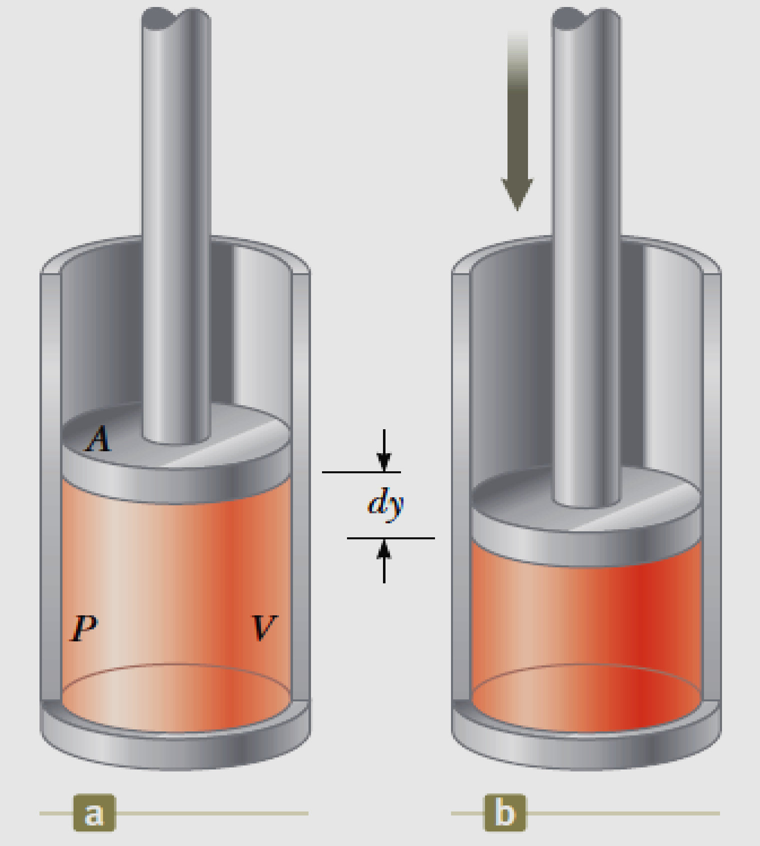


Figure 2: Work is done on a gas contained in a cylinder at a pressure P as the piston is pushed downward so that the gas is compressed.

Work and Heat in Thermodynamic Processes

Where the magnitude F of the external force is equal to PA because the piston is always in equilibrium between the external force and the force from the gas. The mass of the piston is assumed to be negligible in this discussion. Because $A\,dy$ is the change in volume of the gas dV, we can express the work done on the gas as

$$dW = -P\,dV \qquad \text{...............} \ (1)$$

Work and Heat in Thermodynamic Processes

- If the gas is compressed, dV is negative and the work done on the gas is positive.
- If the gas expands, dV is positive and the work done on the gas is negative.
- If the volume remains constant, the work done on the gas is zero.

The total work done on the gas as its volume changes from V_i to V_f is given by the integral of Equation 1:

$$W = -\int_{V_i}^{V_f} P\,dV$$

Work done on a gas

Thermodynamics and Statistical Physics

Dr. Shurooq Saad Mahmood

Lec 8

First Low of Thermodynamics

Work and Heat in Thermodynamic Processes

State variables

In thermodynamics, we describe the state of a system using such variables as pressure, volume, temperature, and internal energy. As a result, these quantities belong to a category called state variables.

State variables describe the state of a system.

For mechanical systems, the state variables include kinetic energy K and potential energy U.

A state of a system can be specified only if the system is in thermal equilibrium internally.

In the case of a gas in a container, internal thermal equilibrium requires that every part of the gas be at the same pressure and temperature.

Work and Heat in Thermodynamic Processes

Transfer variables

A second category of variables in situations involving energy is transfer variables.

Transfer variables are zero unless a process occurs in which energy is transferred across the boundary of a system.

Such a variable has a nonzero value if a process occurs in which energy is transferred across the system's boundary.

The transfer variable is positive or negative, depending on **whether energy is entering or leaving the system**.

Work and Heat in Thermodynamic Processes

Transfer variables

Because a transfer of energy across the boundary represents a change in the system, transfer variables are not associated with a given state of the system, but rather with a change in the state of the system.

- Heat and work are transfer variables.

Work and Heat in Thermodynamic Processes

In the previous sections, we discussed **heat** as a transfer variable. In this section, we study another important transfer variable for thermodynamic systems, **work**.

We investigate the work done on a deformable system, a gas. Consider a gas contained in a cylinder fitted with a movable piston (Figure (2)).

At equilibrium, the gas occupies a volume V and exerts a uniform pressure P on the cylinder's walls and on the piston. If the piston has a cross-sectional area A, the force exerted by the gas on the piston is $F = PA$.

Now let's assume we push the piston inward and compress the gas quasi-statically, that is, slowly enough to allow the system to remain essentially in internal thermal equilibrium at all times.

Work and Heat in Thermodynamic Processes

As the piston is pushed downward by an external force $\vec{\mathbf{F}} = -F\hat{\mathbf{j}}$ through a displacement of $d\vec{\mathbf{r}} = dy\,\hat{\mathbf{j}}$ (Figure (2b)), the work done on the gas is:

$$dW = \vec{\mathbf{F}} \cdot d\vec{\mathbf{r}} = -F\hat{\mathbf{j}} \cdot dy\,\hat{\mathbf{j}} = -F\,dy = -PA\,dy$$

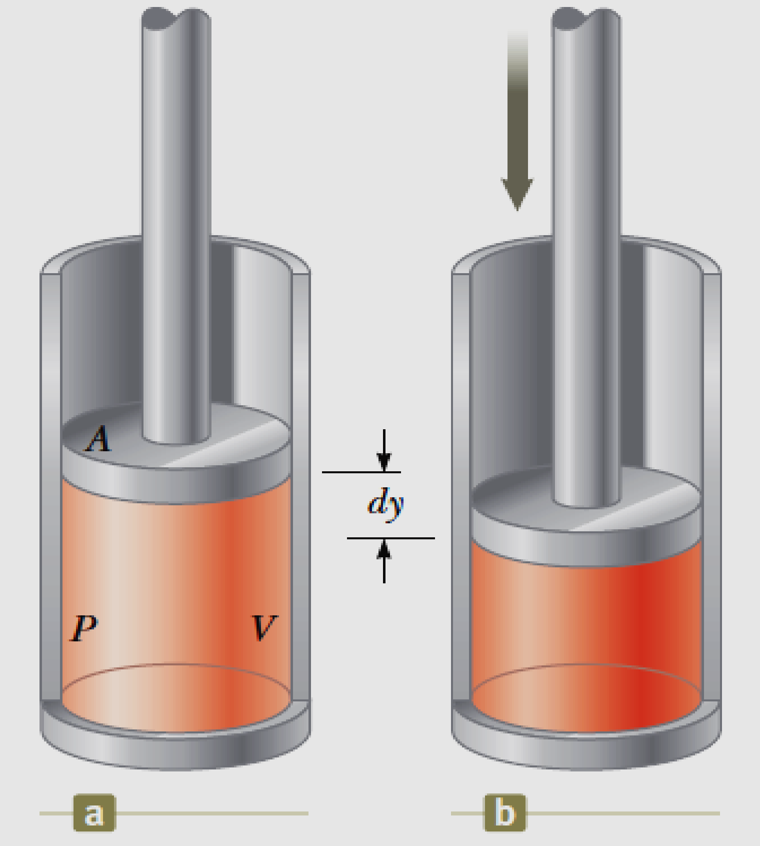


Figure 2: Work is done on a gas contained in a cylinder at a pressure P as the piston is pushed downward so that the gas is compressed.

Work and Heat in Thermodynamic Processes

Where the magnitude F of the external force is equal to PA because the piston is always in equilibrium between the external force and the force from the gas. The mass of the piston is assumed to be negligible in this discussion. Because $A\,dy$ is the change in volume of the gas dV, we can express the work done on the gas as

$$dW = -P\,dV \qquad \text{…………….} \quad (1)$$

Work and Heat in Thermodynamic Processes

- If the gas is compressed, dV is negative and the work done on the gas is positive.
- If the gas expands, dV is positive and the work done on the gas is negative.
- If the volume remains constant, the work done on the gas is zero.

The total work done on the gas as its volume changes from V_i to V_f is given by the integral of Equation 1:

$$W = -\int_{V_i}^{V_f} P\,dV$$

Work done on a gas …………… (2)

Work and Heat in Thermodynamic Processes

To evaluate this integral, you must know how the pressure varies with volume during the process.

In general, the **pressure** is not constant during a process followed by a gas, **but depends on** the volume and temperature. If the pressure and volume are known at each step of the process, the state of the gas at each step can be plotted on a graphical representation called a ***PV* diagram** as in Active Figure 3. This type of diagram allows us to visualize a process through which a gas is progressing.

The curve on a *PV* diagram is called the *path* taken between the initial and final states.

Work and Heat in Thermodynamic Processes

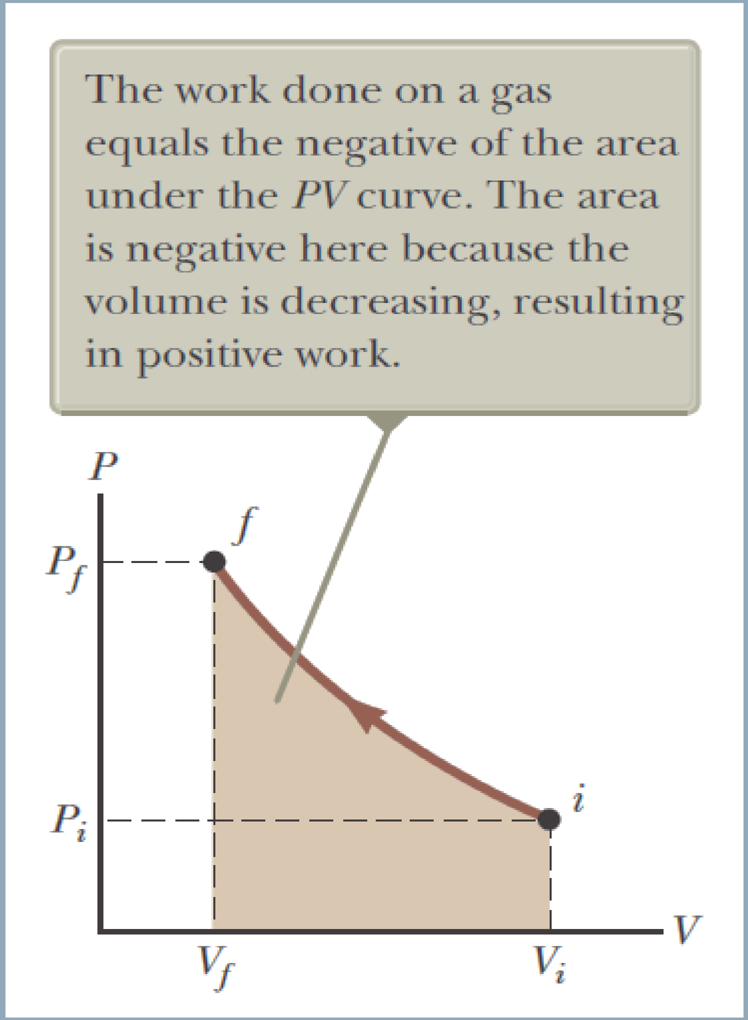
Notice that the integral in Equation 2 is equal to the area under a curve on a *PV* diagram. Therefore, we can identify an important use for *PV* diagrams:

The work done on a gas in a quasi-static process that takes the gas from an initial state to a final state is the negative of the area under the curve on a *PV* diagram, evaluated between the initial and final states.

For the process of compressing a gas in a cylinder, the work done depends on the particular path taken between the initial and final states as Figure 3 suggests.

Work and Heat in Thermodynamic Processes

Figure 3: A gas is compressed quasi-statically (slowly) from state i to state f. An outside agent must do positive work on the gas to compress it.



The work done on a gas equals the negative of the area under the PV curve. The area is negative here because the volume is decreasing, resulting in positive work.

Work and Heat in Thermodynamic Processes

To illustrate this important point, consider several different paths connecting *i* and *f* (Figure 4). In the process depicted in Figure 4a, the volume of the gas is first reduced from V_i to V_f at constant pressure P_i and the pressure of the gas then increases from P_i to P_f by heating at constant volume V_f. The **work done on the gas** along this path is $\boldsymbol{-P_i(V_f - V_i)}$.

In Figure 4b, the pressure of the gas is increased from P_i to P_f at constant volume V_i and then the volume of the gas is reduced from V_i to V_f at constant pressure P_f .

The **work done on the gas** is $\boldsymbol{-P_f(V_f - V_i)}$. This value is greater than that for the process described in Figure 4a because the piston is moved through the same displacement by a larger force.

Work and Heat in Thermodynamic Processes

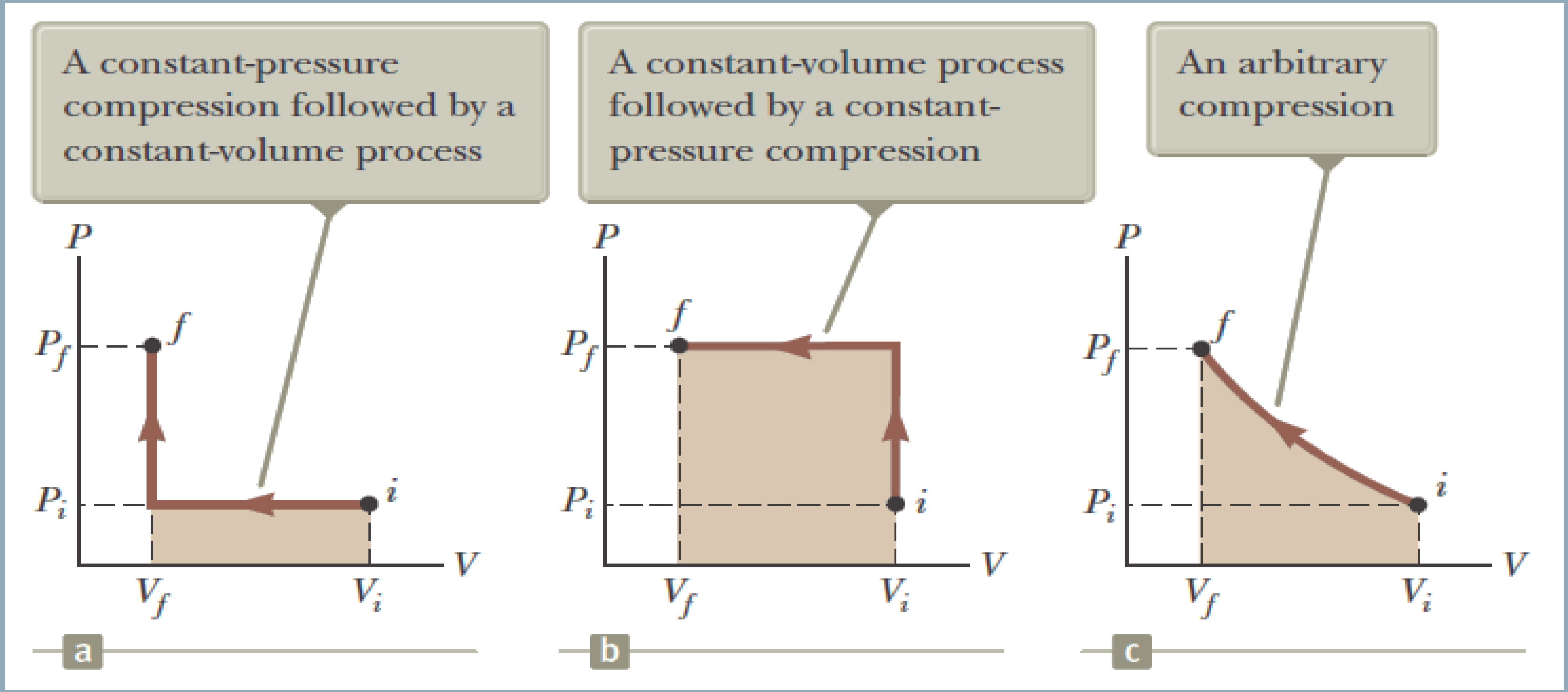


Figure 4: The work done on a gas as it is taken from an initial state to a final state depends on the path between these states.

Work and Heat in Thermodynamic Processes

Finally, for the process described in Figure 4c, where both P and V change continuously, the **work done on the gas** has some value between the values obtained in the first two processes. To evaluate the work in this case, the function $P(V)$ must be known so that we can evaluate the integral in Equation 2.

The First Law of Thermodynamics

The law of conservation of energy: the change in the energy of a system is equal to the sum of all transfers of energy across the system's boundary.

The first law of thermodynamics is a special case of the law of conservation of energy that describes processes in which only the internal energy changes and the only energy transfers are by heat and work:

$$\Delta E_{\text{int}} = Q + W$$ ← **First law of thermodynamics**

An important consequence of the first law of thermodynamics is that there exists a quantity known as internal energy whose value is determined by the state of the system. The internal energy is therefore a state variable like pressure, volume, and temperature.

The First Law of Thermodynamics

Let us investigate some special cases in which the first law can be applied. First, consider an *isolated system*, that is, one that does not interact with its surroundings.

In this case, no energy transfer by heat takes place and the work done on the system is zero; hence, the internal energy remains constant. That is, because $\boldsymbol{Q = W = 0}$, it follows that $\boldsymbol{\Delta E_{\text{int}} = 0}$; therefore, $E_{int,i} = E_{int,\,f}$. We conclude that the internal energy E_{int} of an isolated system **remains constant**.

The First Law of Thermodynamics

Next, consider the case of a system that can exchange energy with its surroundings and is taken through a **cyclic process**, that is, a process that starts and ends at the same state. In this case, the change in the internal energy must again be zero because E_{int} is a state variable; therefore, the energy Q added to the system must equal the negative of the work W done on the system during the cycle. That is, in a **cyclic process**:

$$\Delta E_{\text{int}} = 0 \quad \text{and} \quad Q = -W \quad \text{(cyclic process)}$$

The First Law of Thermodynamics

On a *PV* diagram, a cyclic process appears as a closed curve.

(The processes described in Figure 4 are represented by open curves because the initial and final states differ).

It can be shown that in a cyclic process, the net work done on the system per cycle equals the area enclosed by the path representing the process on a *PV* diagram.