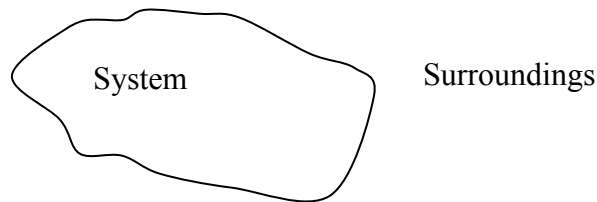


# OUTLINE OF CHAPTER 1

**System**: region under study; a specified volume or a quantity of mass.

**Surroundings**: everything but the system (the rest!).



**State of a System**: “Thermodynamic” state characterized by a set of (macroscopic) variables ( $T$ ,  $P$ ,  $\rho$ , etc).

**Phase**: State of agglomeration of a system (gas, liquid, solid, etc).

**Internal Energy**: Energy associated with the motion (KE), interactions (gravity, electrostatic) and bonding of its constituent molecules.

**External Energy**: Energy associated with the velocity (KE) and location of the center of mass.

**Total Energy**: Internal+ External Energy.

**THERMODYNAMICS RELATES THE INTERNAL ENERGY** (not to its molecular motions and interactions, **BUT**) **TO MACROSCOPIC VARIABLES** (P, T, etc.)

*System is in “**CONTACT**” with surroundings:* If the surroundings can produce a CHANGE in the System.

Mechanical Contact

Change of Pressure (P) in surroundings changes the pressure of the system (among other state properties).

Thermal Contact

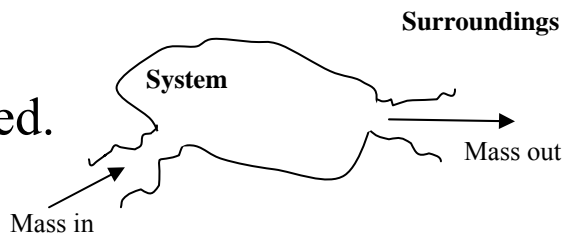
Change of Temperature (T) in surroundings changes the system (not just its T)

Isolated System: No Contact with surroundings

Adiabatic System: No Thermal Contact with surroundings

Closed System: No mass flow from and to the surroundings

Open System: Not closed.



## UNITS: SI System

**Table 1.2-1** The SI Unit System

Unit	Name	Abbreviation	Basis of Definition
Length	meter	m	The distance light travels in a vacuum in 1/299 792 458 second
Mass	kilogram	kg	Platinum-iridium prototype at the International Bureau of Weights and Measures, Sèvres, France
Time	second	s	Proportional to the period of one cesium-133 radiative transition
Electric current	ampere	A	Current that would produce a specified force between two parallel conductors in a specified geometry
Temperature	kelvin	K	1/273.16 of the thermodynamic temperature (to be defined shortly) of water at its triple point (see Chapter 7)
Amount of substance	mole	mol	Amount of a substance that contains as many elementary entities as there are atoms in 0.012 kilogram of carbon-12 ( $6.022 \times 10^{23}$ , which is Avogadro's number)
Luminous intensity	candela	cd	Related to the black-body radiation from freezing platinum (2045 K)

**Table 1.2-2** Derived Units with Special Names and Symbols Acceptable in SI Units

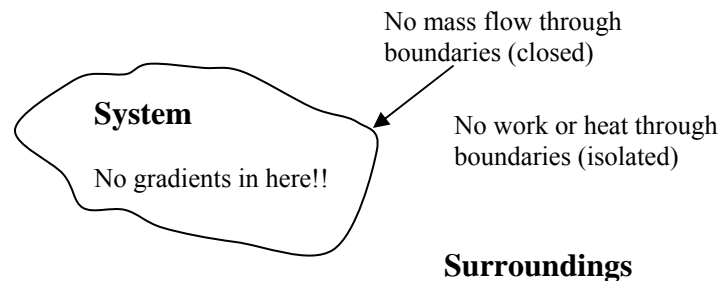
Quantity	Name	Symbol	Expression in	
			SI Units	Derived Units
Force	newton	N	$\text{m kg s}^{-2}$	$\text{J m}^{-1}$
Energy, work, or quantity of heat	joule	J	$\text{m}^2 \text{kg s}^{-2}$	$\text{N m}$
Pressure or stress	pascal	Pa	$\text{m}^{-1} \text{kg s}^{-2}$	$\text{N/m}^2$
Power	watt	W	$\text{m}^2 \text{kg s}^{-3}$	$\text{J/s}$
Frequency	hertz	Hz	$\text{s}^{-1}$	

**Table 1.2-3** Other Derived Units in Terms of Acceptable SI Units

Quantity	Expression in SI Units	Symbol
Concentration of substance	$\text{mol m}^{-3}$	$\text{mol/m}^3$
Mass density ( $\rho = m/V$ )	$\text{kg m}^{-3}$	$\text{kg/m}^3$
Heat capacity or entropy	$\text{m}^2 \text{kg s}^{-1} \text{K}^{-1}$	$\text{J/K}$
Heat flow rate ( $\dot{Q}$ )	$\text{m}^2 \text{kg s}^{-3}$	$\text{W}$ or $\text{J/s}$
Molar energy	$\text{m}^2 \text{kg s}^{-2} \text{mol}^{-1}$	$\text{J/mol}$
Specific energy	$\text{m}^2 \text{s}^{-2}$	$\text{J/kg}$
Specific heat capacity or specific entropy	$\text{m}^2 \text{s}^{-2} \text{K}^{-1}$	$\text{J/(kg K)}$
Specific volume	$\text{m}^3 \text{kg}^{-1}$	$\text{m}^3/\text{kg}$
Viscosity (absolute or dynamic)	$\text{m}^{-1} \text{kg s}^{-1}$	$\text{Pa s}$
Volume	$\text{m}^3$	$\text{m}^3$
Work, energy ( $W$ )	$\text{m}^2 \text{kg s}^{-2}$	$\text{J}$ or $\text{N m}$

**Equilibrium State of a System:** Time invariant and uniform state where flows of heat or mass or work with the surroundings are suppressed.

- **Time invariant:** Does not change with time.
- System is **uniform:** no internal temperature, pressure, velocity or concentration gradients. No changes in concentration due to chemical reactions.



Note 1: With this definition, the book considers only equilibrium of an isolated or closed system.

Note 2 (Effect of time): Isolated systems (no contact) will only become uniform if not at first. Closed systems may have some interactions with the surroundings until they become uniform and time invariant.

**Steady State of an Open System:** Time invariant, possibly non-uniform open systems (e.g. CSTR, PFR). Not of interest in this course.

## ***TWO GENERAL CLASSES OF PROBLEMS IN THERMODYNAMICS***



### Energy Flow Problems

- Computing the work or heat needed for a specific change of state
- Predicting the change of state of a system given the heat and work added/removed.

### Equilibrium Problems

Identify or predict the equilibrium of a system initially NOT at equilibrium.

- Mixing of pure substances
- Opening a valve between two containers with different gases and/or states.

**Natural flows**: Flows of heat, momentum and mass that occur spontaneously.

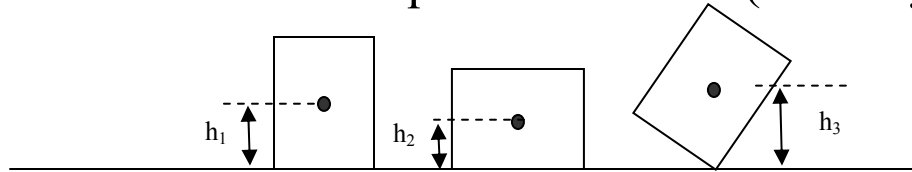
**Forced flows**: Flows of heat, momentum or mass are against the direction of natural flow.

### **OBSERVATIONS**

- Any system free from forced flows will evolve into an equilibrium state.
- Any system at equilibrium will NEVER spontaneously evolve into a non-equilibrium state.

## Types of Equilibrium States:

- **Stable:** small disturbances (small forced flows) change the system but if left alone the system returns to the original state
- **Unstable:** small disturbances make the system evolve to another equilibrium state (unlikely)



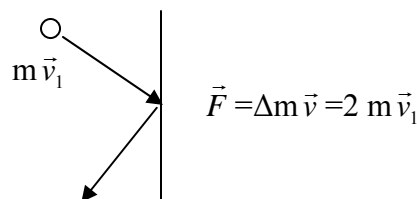
Potential energy:  $mgh_1$        $mgh_2$        $mgh_3$

$mgh_3 > mgh_2$      $mgh_3 > mgh_1$     System needs to go to  $h_3$  to arrive to  $h_2$  from  $h_1$  or vice versa.

- Other examples: Sub-cooled liquids.

## PRESSURE

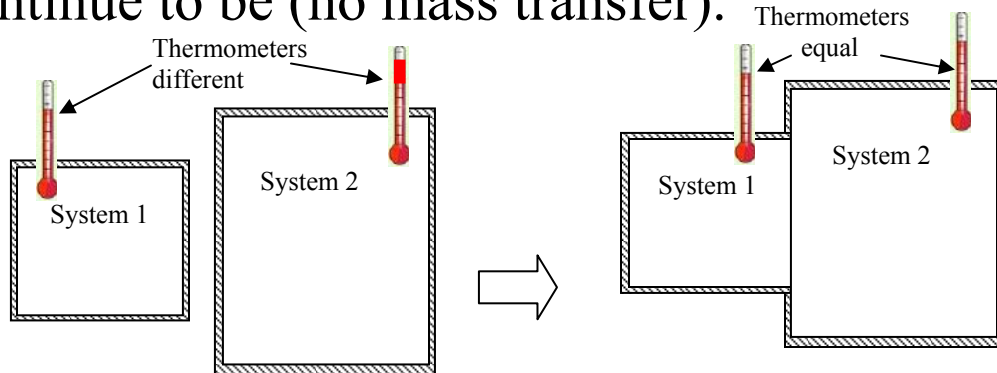
$P = F/A$  (or a bunch of small forces done by molecules on the walls of the system; these forces come from changes of momentum through elastic collisions with the wall)



We refer to pressure as the **ABSOLUTE PRESSURE** (atmospheric + gauge pressure)

# TEMPERATURE

Thermal Equilibrium: Take two isolated system and put them in contact through a RIGID wall (no mechanical work), such as the two systems continue to be (no mass transfer).



Thermometers different  $\Rightarrow$  Thermometers = **Temperature** is therefore defined as **the property that is equal in two systems that are in thermal equilibrium.**

## How about a **scale**??

- Needs to be independent of the device/fluid used.
- Experimental observation: For low density (ideal) gases away from condensation

PV increases with “Hotness”

(something is “hotter” than other if heat flows spontaneously from the hotter to the cooler”)

Thus one can define temperature ( $T'$ ) as follows:

$$PV=A+RT'$$

With  $R$  positive (Recall that  $PV$  increases with “hotness”). In fact, one can redefine  $T=T'+A/R$  and get

$$PV=RT$$

Because  $V>0$ ,  $P>0$ , then  $T>0$ .

Thus, **we need  $R$** , which will give the temperature  $T=PV/R$ , **or the size of a unit of temperature**, which are equivalent



### One Way

Pick a state. Put the gas in contact with it and get  $\underline{PV}$ . Then, assign a temperature  $\underline{T}$  to it. Then  $R = \underline{PV}/\underline{T}$

This leads to an **ABSOLUTE SCALE**

### Other Way

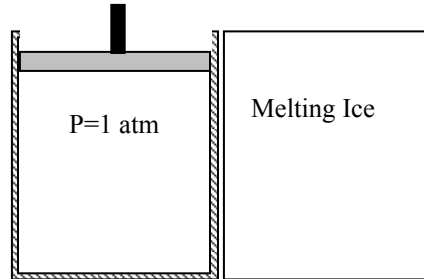
Choose two reproducible states (frozen and boiling water), obtain  $P_1V_1$  and  $P_2V_2$  and then decide how many “degrees” correspond to  $(P_1V_1 - P_2V_2)$ . Choose a “zero”  $T$ . (100 degrees  $\rightarrow$  Celsius scale, 180 degrees  $\rightarrow$  Fahrenheit scale)

This leads to an **ARBITRARY SCALE**, which is what is done.

**Important:**  $R$  needs to be the same for ANY low density gas used. Therefore to have  $PV$  equal for two gases at the same temperature, one needs possibly different amounts of mass of gas to be used. In fact, using this property, one can define the “mole” as the mass needed to make  $PV$  equal for all gases in thermal equilibrium with a specific state.

Indeed. Let us start with assuming a value of  $R$ , say 0.0820574587 (but we will use 0.082).

Then assume we put all gases in contact with ice and wait for thermal equilibrium. We use a piston to accommodate the pressure to be  $P=1 \text{ atm}$ .

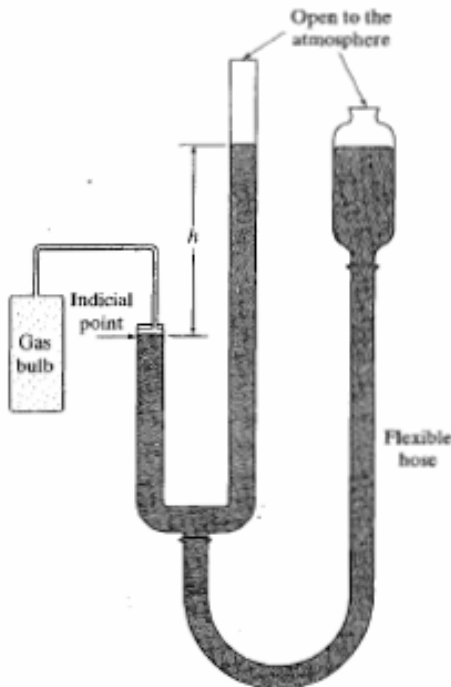


Then  $PV=0.082 T$ . But we decided that  $T=273.16$  for melting ice (common to all gases). Then we will get  $V=0.082 * 273.16 \approx 22.4 \text{ lt}$ . Thus, we can define that a “mol” of gas is whatever amount of gas is needed to fill 22.4 lt at 1 atm and at 273.16 degrees.

Once that is done  $PV=RT$  is known as the “ideal gas scale of temperature”

(We will come back to this in chapter 6).

## IDEAL GAS THERMOMETER



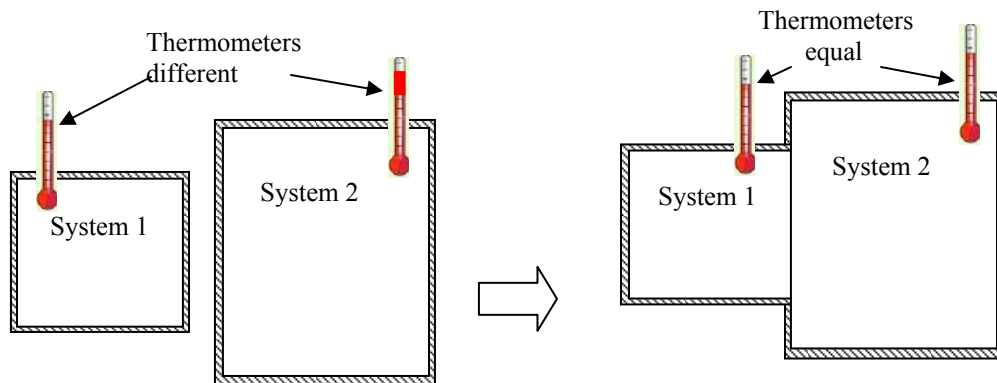
**Figure 1.4-3** A simplified diagram of a constant-volume ideal gas thermometer. In this thermometer the product  $PV$  for a gas at various temperatures is found by measuring the pressure  $P$  at constant volume. For each measurement the mercury reservoir is raised or lowered until the mercury column at the left touches an index mark. The pressure of the gas in the bulb is then equal to the atmospheric pressure plus the pressure due to the height of the mercury column.

(not convenient and replaced by mercury thermometers or others).

# HEAT, WORK AND THE CONSERVATION OF ENERGY

Consider the Thermal Equilibrium example shown before:

(Take two isolated system and put them in contact through a RIGID wall (no mechanical work), such as the two systems continue to be (no mass transfer) )



We say that

Internal Energy of System 1 (before) < Internal Energy of System 1 (after).

Because we define internal energy as being monotone with temperature.

**Therefore: Energy has been transferred from System 2 to System 1. We call this a flow of HEAT**

**Similarly: Energy transfer through mechanical means (piston, stirring, etc) is called WORK**

**Other forms: electricity, radiation, magnetism**

**Mechanical Work: Force×Distance**

**Electrical Work: Current flow×voltage×Time**

# EQUIVALENCY OF HEAT AND WORK

## EXPERIMENTAL OBSERVATION (Joule):

The same amount of energy can always be used to produce the same temperature raise in a given mass of water, regardless of the form (heat, work, etc).

**Experiments that proves it:** Water is put in a dewar at Temperature  $T_1$ , experiments (below) are made, and final temperature  $T_2$  is determined.

Form in Which Energy Is Transferred to Water	Mechanism Used	Form of Energy Supplied to Mechanism	Method of Measuring Energy Input	Corrections That Must Be Made to Energy Input Data
(1) Mechanical energy	Stirring: Paddlewheel driven by electric motor	Electrical energy	Product of voltage, current, and time	Electrical energy loss in motor and circuit, temperature rise of paddlewheel
(2) Mechanical energy	Stirring: Paddlewheel driven by pulley and falling weight	Mechanical energy	Change in potential energy of weight: product of mass of weight, change in height, and the gravitational constant $g$	Temperature rise of paddlewheel
(3) Heat flow	Electrical energy converted to heat in a resistor	Electrical energy	Product of voltage, current, and time	Temperature rise of resistor and electrical losses in circuit
(4) Heat flow	Mechanical energy of falling weight is converted to heat through friction of rubbing two surfaces together, as with a brake on the axle of a pulley	Mechanical energy	Change in potential energy of weight: product of mass of weight, change in height, and $g$	Temperature rise of mechanical brakes, etc.

We expect all the energies (with the corrections) to be the same.

## **OBSERVATIONS:**

**-Energy added to water increased internal energy (molecular motion)**

**-Can calculate the amount of heat (whatever the unit is used) as its equivalent of mechanical work.**

$$1 \text{ Joule} = 1 \text{ N} \cdot \text{m} = \text{xx} \text{ Calories}$$

**“xx” has been chosen by determining the amount of work needed to heat 1 gram of water by 1°C. The amount of heat associated to that is 1 cal.  $\text{xx} = 0.2390 \text{ cal}$**

**-Energy added using one form of energy can be recovered in another!!!!**

## **EQUILIBRIUM STATE SPECIFICATION**

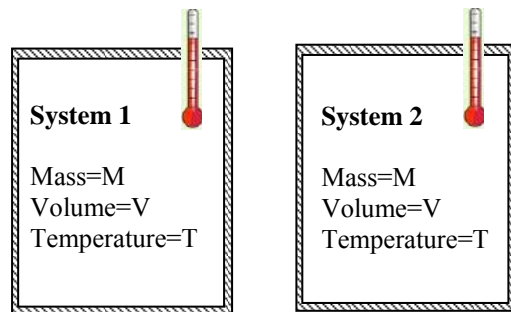
**Question 1: How many variables are needed to specify the equilibrium STATE of a system?**

**Answer: Only by experimental observation at this point.**

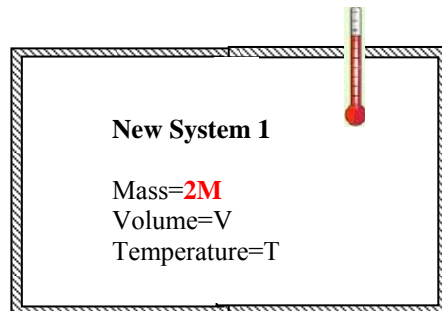
- Single phase one component system (no electrical/magnetic fields): mass and two properties (P, T), or (P, V) or (P, Refractive Index) or (P, density), etc.**
- Multi phase and/or multicomponent (no electrical/magnetic fields): we will see later (chapter 6 and 7).**

## INTENSIVE / EXTENSIVE PROPERTIES

Consider two systems of equal mass, equal volume (V) and equal temperature (same type of mass), and same T



We now put them in contact: Nothing changes, right?  
New system is:



Mass, volume and the energy have doubled, but the other properties (P, T) have not.

**INTENSIVE PROPERTY: Independent of the mass and size of the system**

**EXTENSIVE PROPERTY: Double the mass, double the property.**

## EQUILIBRIUM STATE SPECIFICATION

**STATE VARIABLES: Intensive properties :  $P$  ,  $T$  ,  $\hat{V}$  (specific molar volume)  $\hat{U}$  (specific molar internal energy). We know how to determine number of moles, right?**

**If only two variables are needed to specify a system, then, ALL OTHERS MUST be obtainable from any two.**

$$P = P(T, \hat{V})$$

$$\hat{U} = \hat{U}(T, \hat{V})$$

$$\hat{U} = \hat{U}(T, P)$$

$$\hat{U} = \hat{U}(P, \hat{V})$$

$$P = P(\hat{U}, \hat{V})$$

**$P = P(T, \hat{V})$  is obtained experimentally (Volumetric equation of state). We already know one  $P\hat{V} = RT$  .**

**$\hat{U} = \hat{U}(T, \hat{V})$  is also obtained experimentally (Thermal equation of state).**

# SUMMARY OF IMPORTANT EXPERIMENTAL OBSERVATIONS

## From Chemistry

*Experimental observation 1.* In any change of state (except one involving a nuclear reaction, which is not considered in this book) total mass is conserved.

*Experimental observation 2.* In any change of state total momentum is a conserved quantity.

## From This Chapter

*Experimental observation 3* (Sec. 1.5). In any change of state the total energy—which includes internal, potential, and kinetic energy, heat, and work—is a conserved quantity.

*Experimental observation 4* (Sec. 1.5). A flow of heat and a flow of work are equivalent in that supplying a given amount of energy to a system in either of these forms can be made to result in the same increase in its internal energy. Heat and work, or more generally, thermal and mechanical energy, are not equivalent in the sense

that mechanical energy can be completely converted to thermal energy, but thermal energy can be only partially converted to mechanical energy in a cyclic process.

*Experimental observation 5* (Sec. 1.3). A system that is not subject to forced flows of mass or energy from its surroundings will evolve to a time-invariant state that is uniform or composed of uniform subsystems. This is the equilibrium state.

*Experimental observation 6* (Sec. 1.3). A system in equilibrium with its surroundings will never spontaneously revert to a nonequilibrium state.

*Experimental observation 7* (Sec. 1.3). Equilibrium states that arise naturally are stable to small disturbances.

*Experimental observation 8* (Secs. 1.3 and 1.6). The stable equilibrium state of a system is completely characterized by values of only equilibrium properties (and not properties that describe the approach to equilibrium). For a single-component, single-phase system the values of only two intensive, independent state variables are needed to fix the thermodynamic state of the equilibrium system completely; the further specification of one extensive variable of the system fixes its size.

Other observations are omitted.