1

## LAWS OF THERMODYNAMICS

2

## THERMAL EQUILIBRIUM AND THE ZEROTH LAW OF THERMODYNAMICS

Should have been first

- Two objects placed in thermal contact will eventually come to the same temperature. When they do, we say they are in thermal equilibrium.
- The zeroth law of thermodynamics says that if two objects are each in equilibrium with a third object, they are also in thermal equilibrium with each other.



3

## 13-6 THE GAS LAWS AND ABSOLUTE TEMPERATURE

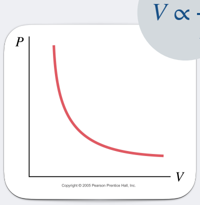
The relationship between the volume, pressure, temperature, and mass of a gas is called an equation of state.

We will deal here with gases that are not too dense.

Boyle's Law:

the volume of a given amount of gas is inversely proportional to the pressure as long as the temperature is constant.

$$V \propto \frac{1}{P}$$






4

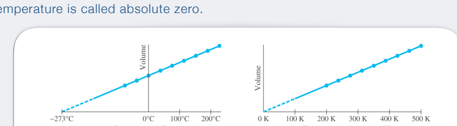
## 13-6 THE GAS LAWS AND ABSOLUTE TEMPERATURE

The volume is linearly proportional to the temperature, as long as the temperature is somewhat above the condensation point and the pressure is constant:

$$V \propto T$$

Extrapolating, the volume becomes zero at −273.15°C;

this temperature is called absolute zero.








5

## 13-6 THE GAS LAWS AND ABSOLUTE TEMPERATURE

The concept of absolute zero allows us to define a third temperature scale – the absolute, or Kelvin, scale.

This scale starts with 0 K at absolute zero, but otherwise is the same as the Celsius scale.

Therefore, the freezing point of water is 273.15 K, and the boiling point is 373.15 K.

Finally, when the volume is constant, the pressure is directly proportional to the temperature:

$$P \propto T$$

6

## 13-7 THE IDEAL GAS LAW

$PV \propto T$

We can combine the three relations just derived into a single relation:

What about the amount of gas present? If the temperature and pressure are constant, the volume is proportional to the amount of gas:

$PV \propto mT$



7

## 13-7 THE IDEAL GAS LAW

- A mole (mol) is defined as the number of grams of a substance that is numerically equal to the molecular mass of the substance:
- 1 mol H2 has a mass of 2 g
- 1 mol Ne has a mass of 20 g
- 1 mol CO2 has a mass of 44 g
- The number of moles in a certain mass of material:

$$n(mol) = \frac{mass(g)}{molecular\ mass(g/mol)}$$



8

## 13-7 THE IDEAL GAS LAW

- We can now write the ideal gas law:

$$\boxed{PV = nRT}$$

- where n is the number of moles and R is the universal gas constant.

$$R = 8.315\ \mathrm{J/(mol \cdot K)} = 0.0821\ \mathrm{(L \cdot atm)/(mol \cdot K)} = 1.99\ \mathrm{calories/(mol \cdot K)}.^{\dagger}$$



9

## 13-8 PROBLEM SOLVING WITH THE IDEAL GAS LAW

- Useful facts and definitions:
- Standard temperature and pressure (STP)

$$T = 273\ \mathrm{K}\ \ (0°\mathrm{C})$$

$$P = 1.00\ \mathrm{atm} = 1.013 \times 10^5\ \mathrm{N/m^2} = 101.3\ \mathrm{kPa}$$

- Volume of 1 mol of an ideal gas is 22.4 L
- If the amount of gas does not change:

$$\boxed{\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}}$$

- Always measure T in kelvins
- P must be the absolute pressure



10

## 13-9 IDEAL GAS LAW IN TERMS OF MOLECULES: AVOGADRO' S NUMBER

- SINCE THE GAS CONSTANT IS UNIVERSAL, THE NUMBER OF MOLECULES IN ONE MOLE IS THE SAME FOR ALL GASES. THAT NUMBER IS CALLED AVOGADRO'S NUMBER:

$$N_A = 6.02 \times 10^{23}$$

- THE NUMBER OF MOLECULES IN A GAS IS THE NUMBER OF MOLES TIMES AVOGADRO'S NUMBER:

$$N = nN_A$$

11

## 13-9 IDEAL GAS LAW IN TERMS OF MOLECULES: AVOGADRO'S NUMBER

- THEREFORE WE CAN WRITE:

$$PV = NkT$$

- WHERE K IS CALLED BOLTZMANN'S CONSTANT.

$$k = \frac{R}{N_A} = \frac{8.315\ \text{J/mol}\cdot\text{K}}{6.02 \times 10^{23}/\text{mol}} = 1.38 \times 10^{-23}\ \text{J/K}$$



12

## 13-10 KINETIC THEORY AND THE MOLECULAR INTERPRETATION OF TEMPERATURE

- Assumptions of kinetic theory:
- large number of molecules, moving in random directions with a variety of speeds
- molecules are far apart, on average
- molecules obey laws of classical mechanics and interact only when colliding
- collisions are perfectly elastic



13

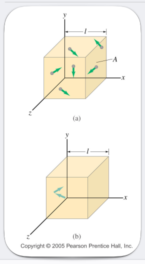
## 13-10 KINETIC THEORY AND THE MOLECULAR INTERPRETATION OF TEMPERATURE

- The force exerted on the wall by the collision of one molecule is

$$F = \frac{\Delta(mv)}{\Delta t} = \frac{2mv_x}{2l/v_x} = \frac{mv_x^2}{l}$$

- Then the force due to all molecules colliding with that wall is

$$F = \frac{m}{l}N\overline{v_x^2}$$






14

## 13-10 KINETIC THEORY AND THE MOLECULAR INTERPRETATION OF TEMPERATURE

- THE AVERAGES OF THE SQUARES OF THE SPEEDS IN ALL THREE DIRECTIONS ARE EQUAL:

$$F = \frac{m}{l}N\frac{\overline{v^2}}{3}$$

$$P = \frac{F}{A} = \frac{1}{3}\frac{Nm\overline{v^2}}{Al} = \frac{1}{3}\frac{Nm\overline{v^2}}{V}$$



15

## 13-10 KINETIC THEORY AND THE MOLECULAR INTERPRETATION OF TEMPERATURE

- Rewriting

$$PV = \frac{2}{3}N\left(\frac{1}{2}m\overline{v^2}\right)$$

- So

$$kT = \frac{2}{3}\left(\frac{1}{2}m\overline{v^2}\right)$$

- And

$$\overline{KE} = \frac{1}{2}m\overline{v^2} = \frac{3}{2}kT$$

The average translational kinetic energy of the molecules in an ideal gas is directly proportional to the temperature of the gas.

16

## 13-10 KINETIC THEORY AND THE MOLECULAR INTERPRETATION OF TEMPERATURE

- We can invert this to find the average speed of molecules in a gas as a function of temperature:

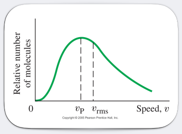
$$v_{\mathrm{rms}} = \sqrt{\overline{v^2}} = \sqrt{\frac{3kT}{m}}$$

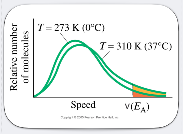
(13-9)



17

## 13-11 DISTRIBUTION OF MOLECULAR SPEEDS



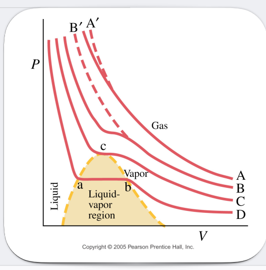

These two graphs show the distribution of speeds of molecules in a gas, as derived by Maxwell. The most probable speed, vP, is not quite the same as the rms speed.

As expected, the curves shift to the right with temperature.



18

## 13-12 REAL GASES AND CHANGES OF PHASE




The curves here represent the behavior of the gas at different temperatures. The cooler it gets, the farther the gas is from ideal.

In curve D, the gas becomes liquid; it begins condensing at (b) and is entirely liquid at (a).

The point (c) is called the critical point.



19

## 13-12 REAL GASES AND CHANGES OF PHASE

Cras Etiam Parturient

Below the critical temperature, the gas can liquefy if the pressure is sufficient; above it, no amount of pressure will suffice.

**TABLE 13–2 Critical Temperatures and Pressures**

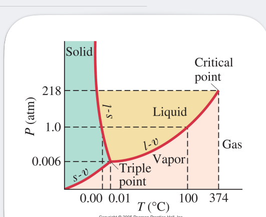
| Substance | Critical Temperature °C | Critical Temperature K | Critical Pressure (atm) |
|---|---|---|---|
| Water | 374 | 647 | 218 |
| $CO_2$ | 31 | 304 | 72.8 |
| Oxygen | −118 | 155 | 50 |
| Nitrogen | −147 | 126 | 33.5 |
| Hydrogen | −239.9 | 33.3 | 12.8 |
| Helium | −267.9 | 5.3 | 2.3 |





20

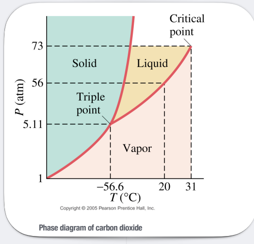
## 13-12 REAL GASES AND CHANGES OF PHASE




Phase diagram of water

A PT diagram is called a phase diagram; it shows all three phases of matter. The solid-liquid transition is melting or freezing; the liquid-vapor one is boiling or condensing; and the solid-vapor one is sublimation.

## 13-12 REAL GASES AND CHANGES OF PHASE




The triple point is the only point where all three phases can coexist in equilibrium.



21

---

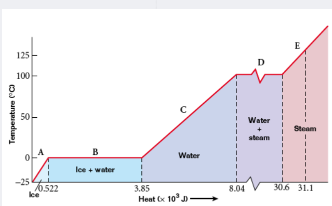
## MORE SLIDES / GRAPHICS

Cras Etiam Parturient



22

---




Changes occurring during the heating of 10.0 g of ice

| Segment of graph | Type of change | Amount of energy transferred by heat | Temperature range of segment |
|---|---|---|---|
| A | temperature of ice increases | 522 J | −25°C to 0°C |
| B | ice melts; becomes water | $3.33 \times 10^3$ J | 0°C |
| C | temperature of water increases | $4.19 \times 10^3$ J | 0°C to 100°C |
| D | water boils; becomes steam | $2.26 \times 10^4$ J | 100°C |
| E | temperature of steam increases | 502 J | 100°C to 125°C |



23

---

## LATENT HEATS OF FUSION AND VAPORIZATION

| Substance | Melting Point (°C) | Melting $L_f$ ( J/kg) | Boiling Point (°C) | Boiling $L_v$ ( J/kg) |
|---|---|---|---|---|
| nitrogen | −209.97 | $2.55 \times 10^4$ | −195.81 | $2.01 \times 10^5$ |
| oxygen | −218.79 | $1.38 \times 10^4$ | −182.97 | $2.13 \times 10^5$ |
| ethyl alcohol | −1 14 | $1.04 \times 10^5$ | 78 | $8.54 \times 10^5$ |
| water | 0.00 | $3.33 \times 10^5$ | 100.00 | $2.26 \times 10^6$ |
| lead | 327.3 | $2.45 \times 10^4$ | 1745 | $8.70 \times 10^5$ |
| aluminum | 660.4 | $3.97 \times 10^5$ | 2467 | $1 .14 \times 10^7$ |



24

---

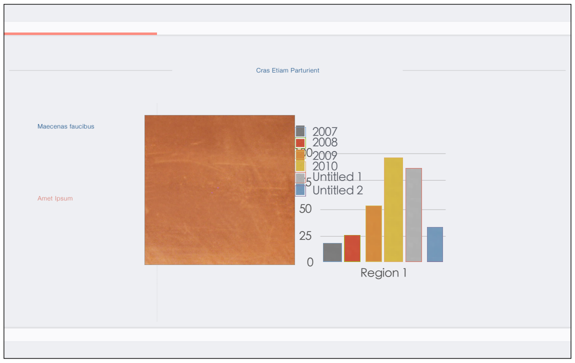
Cras Etiam Parturient

Maecenas faucibus

Amet Ipsum


25

26


Cras Etiam Parturient
Maecenas faucibus
Amet Ipsum
2007
2008
2009
2010
Untitled 1
Untitled 2
50
25
0
Region 1