### Chapter 19 Entropy

### $\frac{\text{PRINCIPLES & PRACTICE OF}}{PHYSICS}$

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### Ch 19 & 20 material

#### What to focus on?

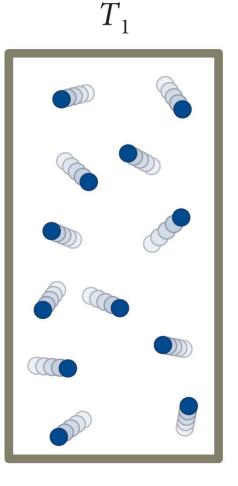
- Just put out some practice problems
- Ideal gas how to find P/V/T changes.
  - E.g., "gas scaling," "intro to the ideal gas law," "pressure cooker," 19.6
- How to calculate energy required for a given T rise
  - E.g., 20.15, 20.16, 20.19, 20.20

#### **Section Goals**

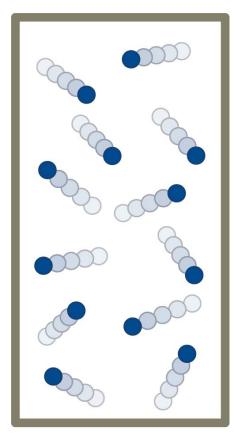
You will learn to

- Relate the microscopic and macroscopic
   parameters that describe an ideal gas.
- Derive the ideal gas

   law and the
   relationship between
   thermal energy and
   temperature.



$$T_2 > T_1$$



- We will now connect some of the atomic parameters that describe an ideal gas to its macroscopic parameters.
- Consider a monatomic gas that consists of a very large number N of indistinguishable atoms of mass m inside a closed rigid container of volume V.
- The figure shows one atomwall collision.
- All collisions are elastic.



Velocity component  $\cdots$   $\vec{v}_{x,f}$ perpendicular to wall reverses direction.  $\vec{v}_{f}$   $\vec{v}_{y,f}$ 

Component parallel to wall does not change.

#### Checkpoint 19.24

**19.24** Let the system comprising the atoms and wall in Figure 19.25 be isolated.

(*a*) What is the direction of the atom's change in momentum?

Perpendicular to wall, to left

(*b*) What is the direction of the change in momentum of the wall?

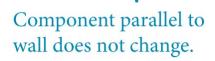
#### Opposite the atom

(c) How are these momentum changes related to the forces that wall and atom exert on each other?

#### Force is proportional!



Velocity component ••••• perpendicular to wall reverses direction.



 $\vec{v}_{v}$ 



 $ec{v}_{
m y,i}$ 

n

 $ec{v}_{\mathfrak{c}}$ 

 $\vec{v}_{x,i}$ 

• If  $\vec{F}_{gA}^{c}$  is the force exerted by the gas on the wall of surface area *A*, then using the definition of pressure we can write

$$P \equiv \frac{F_{gA}^{c}}{A} = \frac{F_{Ag}^{c}}{A}$$

- The force exerted by the wall on the gas  $\vec{F}_{Ag}^{c}$  is equal to the rate of change of momentum of the gas.
- From Figure 19.25, we can determine that the magnitude of the atom's change in momentum is  $2m|v_x|$ .
- We need to determine how many collisions occur in time  $\Delta t$ .

- For the atom to collide with the wall in time  $\Delta t$ , it has to be within a distance  $|v_x|\Delta t$ .
- On average, only one half of the atoms in the cylinder of volume  $A|v_x|\Delta t$  will strike the wall in time  $\Delta t$ .
- The number of atoms in the cylinder is

 $N_{\rm cyl} = (N/V)A |v_x| \Delta t.$ 

• The change in momentum for all gas collisions in time  $\Delta t$  is

$$\left|\Delta p\right| = \frac{1}{2} \frac{N}{V} (A \left| v_x \right| \Delta t) (2m \left| v_x \right|) = \frac{NAmv_x^2}{V} \Delta t$$

• Now we can obtain for the pressure in the gas:

$$P = \frac{\left|\Delta p\right| / \Delta t}{A} = \frac{Nmv_x^2}{V}$$

• Using  $v_{\text{rms}}^2 = 3(v_x^2)_{\text{av}}$ , (same *v* in all 3 directions on average) we get  $P = \frac{Nm\frac{1}{3}v_{\text{rms}}^2}{V} = \frac{2}{3}\frac{N(\frac{1}{2}mv_{\text{rms}}^2)}{V}$ 

• Now substituting 
$$E_{\text{th}} = N\left(\frac{1}{2}mv_{\text{rms}}^2\right)$$
,  
 $P = \frac{2}{3}\frac{E_{\text{th}}}{V}$  (monatomic ideal gas)

- Thermal energy?
  - Long story short: an object gets  $\frac{1}{2}k_{\rm B}T$  worth of thermal energy from its surroundings on average *per degree of freedom*
  - Point particle: free to move in 3 directions
  - Molecule? Add possible rotations too
  - Aside from details,  $E_{\rm th} \sim T$  defines temperature
- So: for *N* single atoms in 3 dimensions, average thermal energy known:

$$E_{\rm th} = \frac{3}{2} N k_{\rm B} T$$
 (monatomic ideal gas)

• From equations 19.50 and 19.48 we obtain the **ideal gas law**:

$$P = \frac{N}{V} k_{\rm B} T \quad \text{(ideal gas system at equilibrium)}$$

• Because thermal energy of a gas is the sum of the average kinetic energies of its atoms ( $E_{th} = NKav$ ), we can write

$$K_{\rm av} = \frac{1}{2} m v_{\rm rms}^2 = \frac{3}{2} k_{\rm B} T$$

• The equation allows us to express the rms speed of an atom in a monatomic gas:

$$v_{\rm rms} = \sqrt{\frac{3k_{\rm B}T}{m}}$$

#### Checkpoint 19.26

**19.26** A certain number of helium atoms are placed in one container, and an equal number of argon atoms are placed in a separate identical container. The pressure is the same in both containers. Helium atoms have a smaller mass than argon atoms. For which gas, if either, (*a*) is the thermal energy smaller, (*b*) is the average kinetic energy of an atom smaller, (*c*) is the rms speed of an atom smaller?

- (a) Neither P & V are the same, so T is the same, and then so is thermal energy.
- (b) Same number of atoms, same thermal energy, so same per atom

(c) Argon – same KE, but it is heavier

### Section 19.7 Question 7

What two atomic parameters determine the pressure in a monatomic ideal gas?

- 1. Absolute pressure
- 2. Atomic mass
- 3. Average kinetic energy
- 4. Atomic radius
- 5. Number density
- 6. Average potential energy
- 7. Force of gravitational attraction

### Section 19.7 Question 7

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- ✓ 3. Average kinetic energy
  - 4. Atomic radius
- ✓ 5. Number density
  - 6. Average potential energy
  - 7. Force of gravitational attraction

A bag of potato chips contains 2.00 L of air when it is sealed at sea level at a pressure of 1.00 atm and a temperature of 20.0°C.

What will be the volume of the air in the bag if you take it with you, still sealed, to the mountains where the temperature is 7.00°C and atmospheric pressure is 70.0 kPa?

Assume that the bag behaves like a balloon and that the air in the bag is in thermal equilibrium with the outside air. (1 atm =  $1.01 \times 10^5$  Pa)

#### Problem 19.6

Number of atoms is constant, so solve idea gas equation for that. The resulting quantity is the same initially and finally. That's basically it.

$$nR = const = \frac{pV}{T} \implies \frac{p_iV_i}{T_i} = \frac{p_fV_f}{T_f}$$

Watch the units. Always use K for temperature.

#### **Chapter 19: Summary**

# Quantitative Tools: Properties of a monatomic ideal gas

• The pressure in a monatomic ideal gas containing *N* atoms at an absolute temperature *T* and occupying a volume *V* is

$$P = \frac{2}{3} \frac{E_{\text{th}}}{V},$$

and the thermal energy of the gas is

$$E_{\rm th} = \frac{3}{2} N k_{\rm B} T.$$

• The **ideal gas law** applied to the gas is

$$P = \frac{N}{V} k_{\rm B} T.$$

#### **Chapter 19: Summary**

# Quantitative Tools: Properties of a monatomic ideal gas

• The average kinetic energy of its atoms is

$$K_{\rm av} = \frac{1}{2} m v_{\rm rms}^2 = \frac{3}{2} k_{\rm B} T,$$

where m is the mass of each atom, and their rootmean-square speed is

$$v_{\rm rms} = \sqrt{\frac{3k_{\rm B}T}{m}}$$

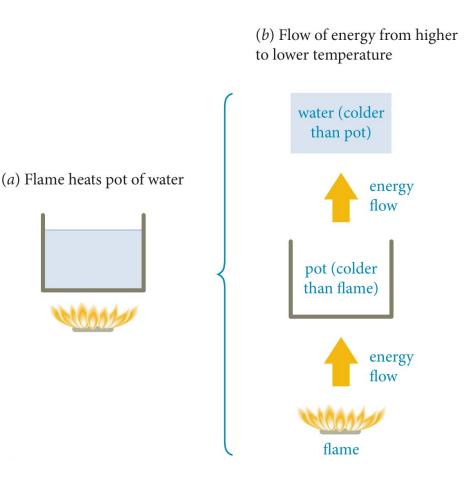
### Chapter 20 Energy Transferred Thermally

 $\frac{\text{PRINCIPLES} \And \text{PRACTICE OF}}{PHYSICS}$ 

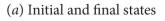
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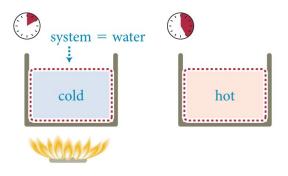
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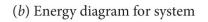
- When two objects that are not at the same temperature are in contact with each other, energy is transferred from the higher-temperature ("hotter") object to the lowertemperature ("cooler") object. <sup>(a)</sup>
- We attribute this transfer of energy to a **thermal interaction** between the objects.
- As the lower-temperature object gets hotter, its thermal energy increases.

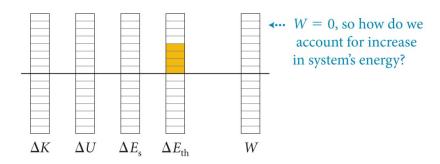


- Consider the water in the figure as our system.
- Because there is no work done on the system, the energy diagram for the system is incomplete.
- To complete the energy diagram, we need to account for the energy transfer due to the thermal interaction.



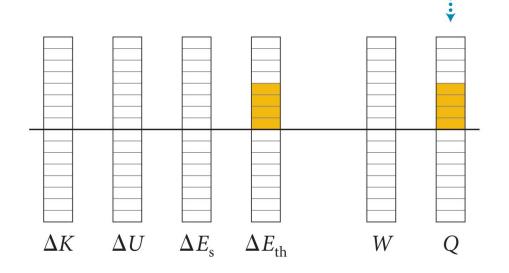






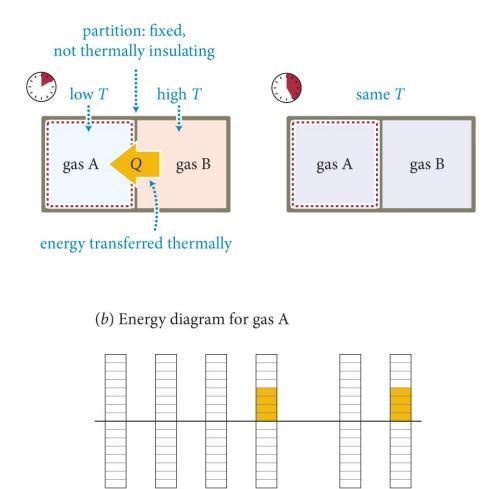
- The amount of energy transferred thermally is denoted by the letter Q.
- *Q* is generally referred to as *heat*.
- Calling it heat is misleading, it incorrectly suggests that heat is a property of an object. It is just another form of energy, ultimately kinetic.
- Better: use the term **energy transferred thermally** to refer to *Q*.

Bar accounts for energy transferred thermally to system.



- Consider the situation shown in the figure.
- The gasses interact thermally, and energy is transferred from B to A.
- If energy is transferred into the system, Q is positive.
- If energy is transferred out of the system, Q is negative.
- Energy will be transferred until an equilibrium *T* is reached

(a) Gases at different temperatures are placed in thermal contact



 $\Delta K$ 

 $\Delta U$ 

 $\Delta E_{\rm s}$ 

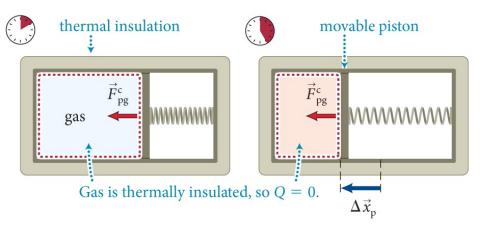
 $\Delta E_{\rm th}$ 

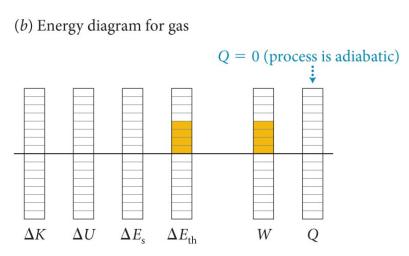
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W

- The thermal energy of a system can be changed either by transferring energy thermally or by doing work on the system.
- A process that does not involve any thermal transfer of energy (Q = 0) is called an adiabatic process.
- This is mostly what we've worried about

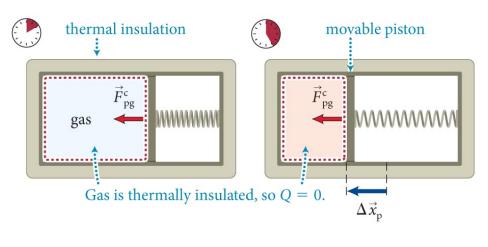
(a) Spring-loaded piston compresses thermally insulated ideal gas



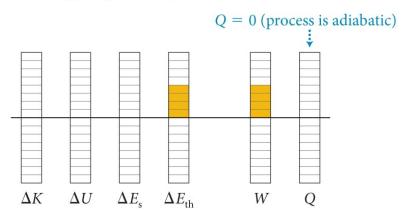


- When the volume of a gas decreases, the work done on the gas is positive.
- When the volume increases, the work done on the gas in negative.
- When there is no change in volume, the work done on the gas is zero.

(a) Spring-loaded piston compresses thermally insulated ideal gas



(b) Energy diagram for gas



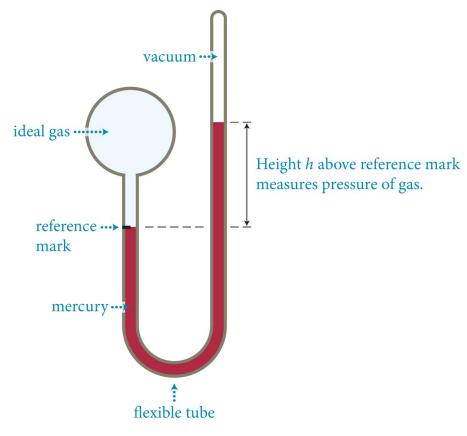
#### Transferring energy to a system Go back and read this carefully later.

	DOING WORK	TRANSFERRING ENERGY THERMALLY
Technical term:	Mechanical interaction between system and its environment	Thermal interaction between system and its environment
Mediated by:	Macroscopic pushes and pulls	Atomic collisions
Requires:	A nonzero external force $\vec{F}_{ext}$ exerted on the system and a nonzero force displace- ment $\Delta \vec{x}_F$	A nonzero temperature difference $\Delta T$ be- tween the system and its environment.
Amount of energy transferred <i>into</i> system:	<i>W</i> ("work done on system")	<i>Q</i> ("energy transferred thermally to system")
Sign:	W > 0 when external force and force displacement are in the same direction (energy of system increases in absence of other transfers)	Q > 0 when environment is at a higher temperature than system (energy of system increases in absence of other transfers)
	W < 0 when external force and force displacement are in opposite directions (energy of system decreases in absence of other transfers)	Q < 0 when environment is at a lower temperature than system (energy of system decreases in absence of other transfers)
Equilibrium:	The vector sum of the external forces is zero, and the force displacement of each external force is zero (mechanical	System is at same temperature as its environ- ment (thermal equilibrium)
	equilibrium)	Text: p. 532

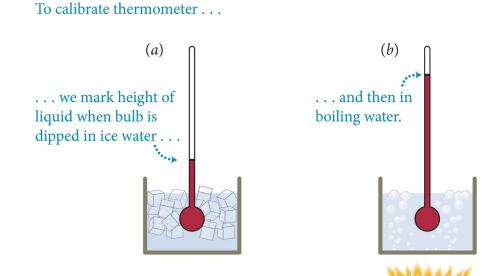
#### **Section Goals**

#### You will learn to

- Establish the measurement of temperature using a **gas thermometer** and how to calibrate it experimentally.
- Define the **triple-point of water** and **absolute zero** both physically and using pressure-temperature graphs.

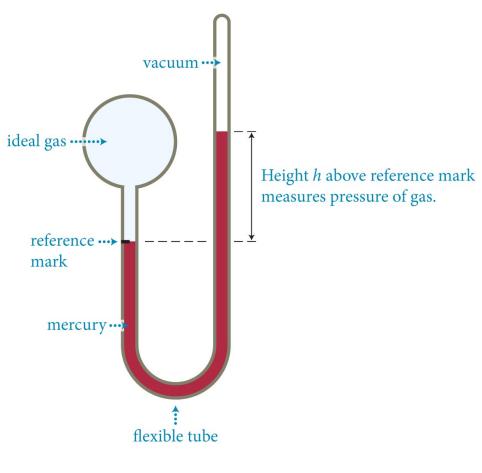


- Any physical property that changes with temperature can be used as a thermometer.
- In a glass thermometer, shown in the figure, a small volume of liquid expands or contracts when placed in contact with a "hot" or "cold" object.
- The object's temperature is determined by the length of the column of liquid.

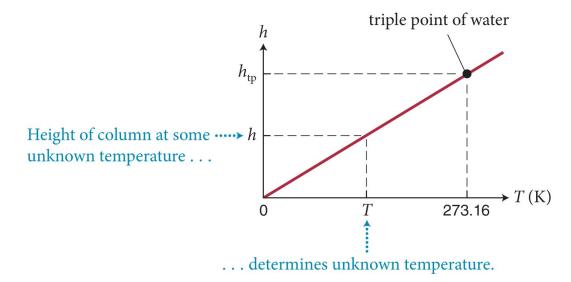


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- The figure illustrates the basic principle of an ideal gas thermometer, which measures the pressure in a gas kept enclosed in a fixed volume.
- For a fixed value of V, the ideal gas law,  $P = Nk_{\rm B}T/V$ , tells us that the pressure P is proportional to the absolute temperature T.
- The height *h* of the mercury column above the reference point measures the temperature.



- The current standard of absolute temperature is based on the **triple point of water**.
- At the triple point, liquid water, solid ice, and water vapor coexist in thermal equilibrium.
- For historical reasons, the absolute temperature at the triple point of water is set to  $T_{tp} \equiv 273.16$  K.
- Zero temperature (T = 0 K) is called **absolute zero**.
- From ideal gas law, when T = 0, P = 0.



#### Table 20.1 Comparison of temperature scales (defining points in bold)

Temperature	Kelvin (K)	Celsius (°C)	Fahrenheit (°F)
Absolute zero	0	-273.15	-459.67
Water freezes (at a pressure of 101.325 kPa)	273.15	0	32
Triple point of water	273.16	0.01	32
Room temperature	293	20	68
Average human body temperature	310	37.0	98.6
Water boils (at a pressure of 101.325 kPa)	373.12	100	212
Titanium melts	1941	1668	3034
Surface of the Sun	5778	5505	9941

#### How to convert? Google. "20C in K" Fahrenheit is not a thing we do.

#### **Section Goals**

You will learn to

- Establish the extensive quantity **heat capacity** and its mathematical representation. Heat capacity is the amount of energy needed to change the temperature of a given amount of a substance.
- Derive the related intensive quantity **specific heat capacity**, which is size independent.
- Recognize familiar patterns of nature such as the rapid cooling of sand and the slow cooling of water at the beach after sunset are a consequence of the differing specific capacities of sand and water.

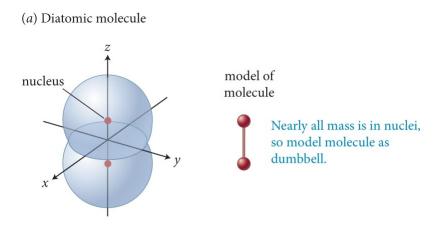
- Specific heat capacity, denoted by letter *c*, is a measure of how much energy is required to raise the temperature of 1 kg of a certain material by 1 K.
- SI units of c are J/K  $\cdot$  kg.
- To understand why the heat capacities of materials are so different from each other, let us first examine ideal gases.

Material	$c (J/K \cdot kg)$	
alcohol	2436	
aluminum	897	
brass	385	
carbon graphite	685	
copper	385	
glass	837	
gold	130	
helium	3116	
ice (268 K)	2090	
iron	449	
lead	130	
marble	860	
mercury	140	
nickel	443	
platinum	133	
silver	235	
steam (373 K)	1556	
titanium	527	
water	4181	
wood	1700	
zinc	388	

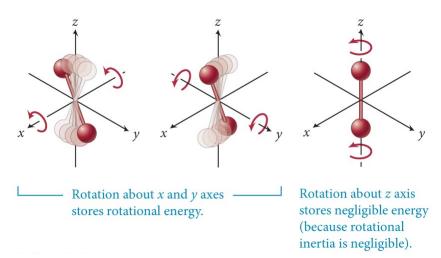
All values are reported at a temperature of 298 K (unless otherwise noted) and atmospheric pressure and with the gases held at constant volume.

- As we saw in Chapter 19, each atom in a monatomic gas has an average thermal energy equal to  $\frac{3}{2}k_{\rm B}T$ .
- Atoms in a monatomic gas are free to move along the *x*, *y* and *z* axes.
- These atoms carry energy exclusively as translational kinetic energy (3 degrees of freedom).
- Molecules in different gases may have additional modes of energy storage associated with vibration or rotational motion.
- We define the number of **degrees of freedom** as the number of independent ways of storing energy in a particle.

- In an ideal gas, each particle's equipartition energy share of the energy of the gas is 1/2 dk<sub>B</sub>T, where d is the number of degrees of freedom.
- So, each atom of a monatomic gas has energy equal to  $3(\frac{1}{2}k_{\rm B}T)$ .
- The dumbbell-shaped hydrogen molecule shown has two additional "rotational degrees of freedom" for a total of five.
- Hydrogen has thermal energy per molecule equal to  $\frac{5}{2}k_{\rm B}T$ .







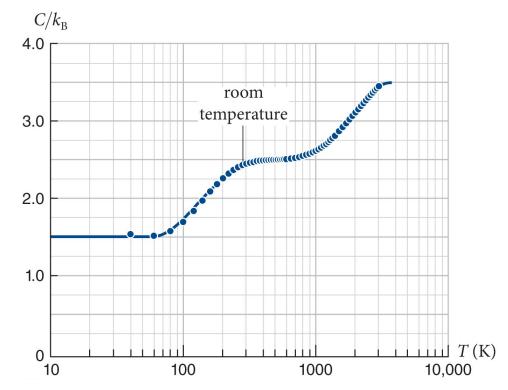
- If we raise the temperature of a monatomic ideal gas by 1 K, the thermal energy of each atom goes up by  $\frac{3}{2}k_{\rm B}T$ .
- Therefore, we expect the heat capacity per atom to be  $\frac{3}{2}k_{\rm B}$ .
- Heat capacities per particle (denoted by *C*) in units of k<sub>B</sub> for a number of substances are listed in the table.
- Note water is weird. Hydrogen bonding.

#### Table 20.3 Heat capacities per particle in units of $k_B$

Class	Material	$C_V/k_{ m B}$
Monatomic gases	helium	1.50
	argon	1.50
	krypton	1.50
	xenon	1.51
	radon	1.51
Polyatomic gases	ammonia	3.37
	hydrogen	2.47
	nitrogen	2.50
Liquids	mercury	3.38
	water	8.97
Solids	aluminum	2.91
	copper	2.94
	gold	3.08
	iron	3.02
	silver	3.05
	titanium	3.04
	zinc	3.05

All values are reported at a temperature of 298 K and atmospheric pressure and with gases held at constant volume (as indicated by the subscript V on  $C_V$ ).

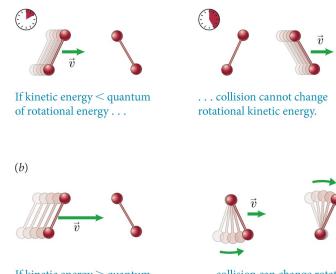
• The figure shows the temperature dependence of the heat capacity per particle for hydrogen gas molecules.



• The reason why *diatomic* hydrogen gas behaves like a *monatomic* gas at low temperatures can be explained using quantum mechanics.

- On small scales, energy is discrete (quantum). Molecules vibrate with only certain specific resonance frequencies, like standing waves.
- Only degrees of freedom for which  $\frac{1}{2}k_{\rm B}T$  is greater than the quantum of energy associated with that degree of freedom contribute to the heat capacity of a gas.
- That means you can 'freeze out' some degrees of freedom at low temperature, since you don't have enough energy to excite them. This lowers the heat capacity <sup>(a)</sup>

In thermal equilibrium, each contributing degree of freedom of a particle in an ideal gas stores  $\frac{1}{2}k_{\rm B}T$  of thermal energy.

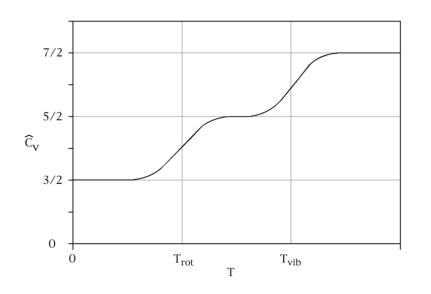


If kinetic energy > quantum of rotational energy . . .

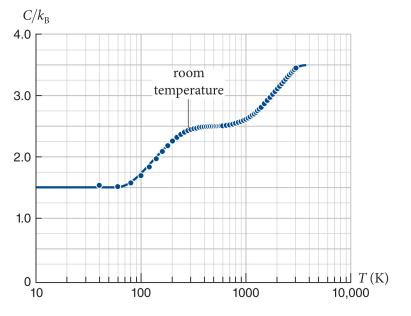
... collision can change rotational kinetic energy.

#### Ideal diatomic gas vs hydrogen

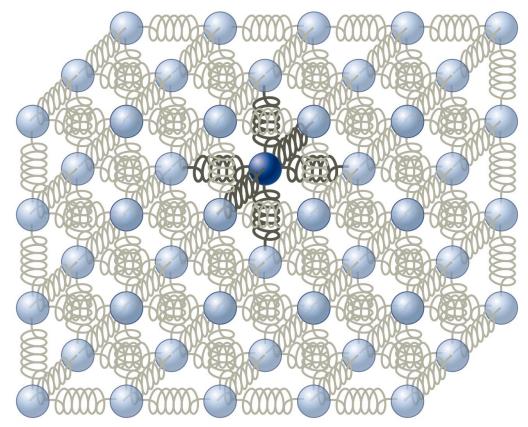
- High T: translation + rotation + vibration
- Middle T: freeze out vibration (higher energy, lose 2 d.f.)
- Low T: freeze out rotation (medium energy, lose 2 d.f.)
- Lowest T: only translation left, 3 directions = 3 d.f.



Ideal diatomic https://en.wikipedia.org/wiki/Heat\_capacity



- Consider the simple arrangement of atoms in a solid crystal.
- Each atom can vibrate along the three axes of the crystal.
- Vibration along each axis contributes 2 degrees of freedom, for a total of 6.
- Therefore, we expect the heat capacity per atom of a solid to be  $3k_{\rm B}$ .
- This is in agreement with experimental measurements.



#### **Checkpoint 20.8**

**20.8** Two identical volumes of gases—one monatomic and the other diatomic—are at the same pressure at room temperature. The temperature of each is raised by the same amount by thermally transferring energy to each of them. Is the energy transferred to the monatomic gas smaller than, equal to, or greater than the energy transferred to the diatomic gas?

Less than. More energy must be transferred to the diatomic gas because it has more degrees of freedom (and each needs some energy), so its heat capacity per particle is greater.

Diatomic = Bigger heat capacity = larger energy required for same temp rise

#### **Chapter 20: Energy Transferred Thermally**

#### **Quantitative Tools**

#### Calculating how hot stuff gets

- Heat energy is Q = mcT, where c is heat capacity
- *c* is how much heat energy can flow per unit temperature difference per unit mass, J/kg-K
- So long as P and V do not change (no work done), heat is the only energy change.
- That means in the absence of phase transitions (e.g., melting/freezing or boiling/condensing), the energy input required for a given temperature rise is

$$E = Q = mc\Delta T$$

• (problems 20.15, 20.16, 20.19)

#### How hot stuff gets

- If you have 2 objects in contact? Thermal energy (heat) is transferred from hot to cold until equilibrium is reached.
- If the two are in contact but isolated from surroundings, the net change in energy is zero.

• (Problem 20.20)

• Say we have a hot thing (H) and a cold thing (C) in contact. Energy conservation gives

$$\Delta Q_{H} + \Delta Q_{C} = 0$$
  
$$m_{h}c_{H}(T_{H} - T_{eq}) + m_{C}c_{C}(T_{C} - T_{eq}) = 0$$
  
$$\implies T_{eq} = \frac{m_{H}c_{H}T_{H} + m_{C}c_{C}T_{C}}{m_{H}c_{H} + m_{C}c_{C}}$$

#### What if stuff melts or boils?

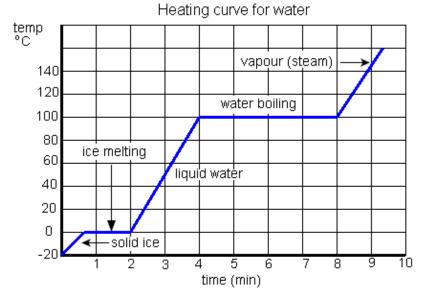
- At the phase change, energy added doesn't change T at all, it goes into breaking bonds and changing phase
- Before the phase change, you pay energy to raise temperature.
- At the phase change, you pay a toll: you have to give a certain amount of energy to accomplish the phase change before you can heat the new phase
- How much?

### $Q_{\rm transform} = L \mathfrak{m}$

• *L* = latent heat. Vaporize/condense or fuse/melt

#### Ice to water

- Heat ice. Melts at 273K, heat from  $T_i$ 
  - $Q = c_i m(T_i 273 \text{K})$
- Melt ice. No T change.
  - $Q = L_f m$
- Heat water up to boiling point.
  - $Q = c_w m(373 \text{K} 273 \text{K})$
- Boil water. No T change.
  - $Q = L_v m$
- Heat steam
  - $Q = c_s m(T_f 373 \text{K})$



### Second to last things

- Work problems for the final.
- Look through the end of chapter formulas to make sure you know they are good for. You'll have a formula sheet, but its no use if you don't know the meaning of the formulas.
- Sleep before the final. Being sharp is better than cramming, this stuff is not about memorization.
- The final is right here, 11:30 on Tuesday. Bring **pencils** and calculators. If you are running late, still show up.

#### Last things

- Do your Student Opinion of Instruction (SOI) survey
- Ask questions now while you have us here.
- Extra credit for post-test: up to 0.5% added to final grade. If you got 50% on the post test, you get 0.25% added on. I will post these grades. You did extremely well compared to historical norms.