

# Gas Processes and Heat Transport

## Physics 1425 Lecture 34

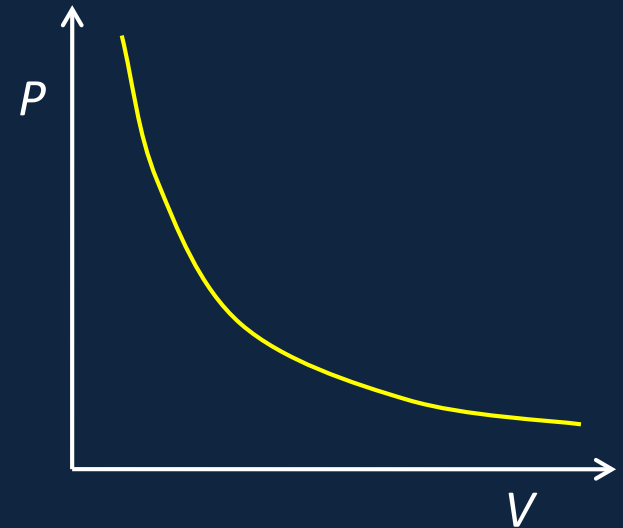
# The First Law of Thermodynamics

- A closed system has a total internal energy  $E_{\text{int}}$ .
- This energy can be changed in two different ways:
  - A. The system can do **work  $W$** , or have work done on it,  $-W$ .
  - B. **Heat  $Q$**  can flow into the system, or  $-Q$  flow out.
- The First Law is just total energy conservation:

$$\Delta E_{\text{int}} = Q - W$$
- **Change in internal energy = heat in – work done.**

# States of an Ideal Gas

- Suppose we have  $n$  moles of an ideal gas in equilibrium in a piston. The “state” of the gas can be defined by giving the **state variables  $P, V$** . The gas state is a point in the  $(P, V)$  plane.
- If heat is exchanged or work done, the gas state variables **trace a path** in the  $(P, V)$  plane.
- If the gas moves along an **isotherm  $PV = \text{constant}$** , its internal energy stays the same.

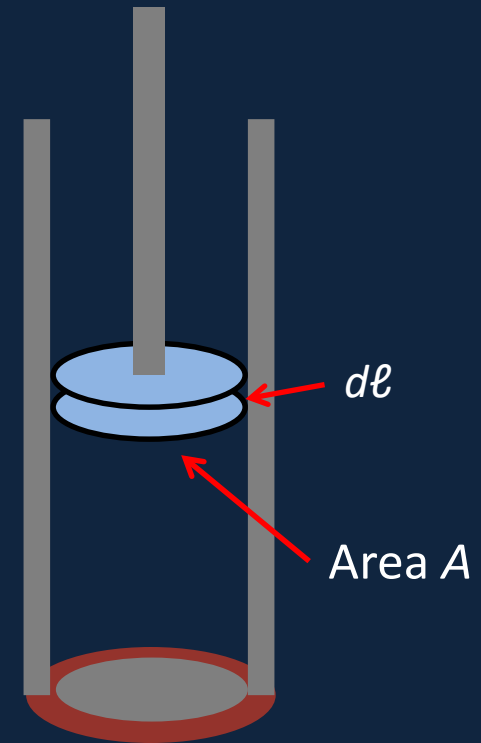


The temperature (and therefore internal energy) is constant along an isotherm,  $PV = \text{const.}$

# The Gas Does Some Work

- The gas pressure  $P$  means the force from the gas on the piston, of area  $A$ , is  $PA$ . This means that if the piston moves up a distance  $d\ell$ , the work done by the gas, force  $\times$  distance =  $PA d\ell = PdV$ .
- The work done by the gas in expanding **isothermally**, along  $PV = nRT$ , is

$$W = \int_{V_A}^{V_B} PdV = \int_{V_A}^{V_B} \frac{nRT}{V} dV = nRT \ln \frac{V_B}{V_A}$$



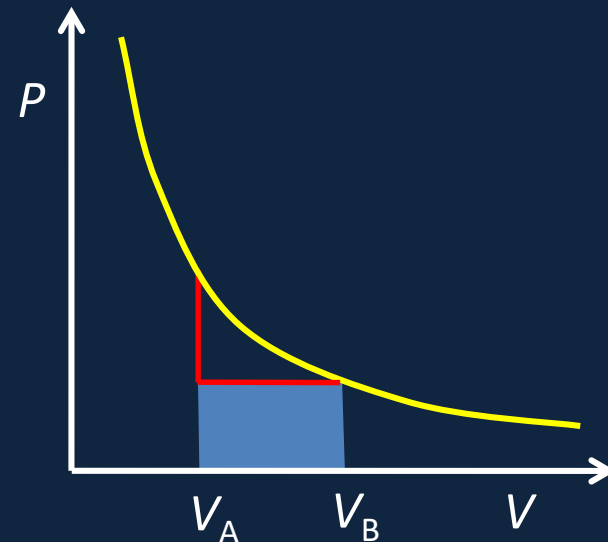
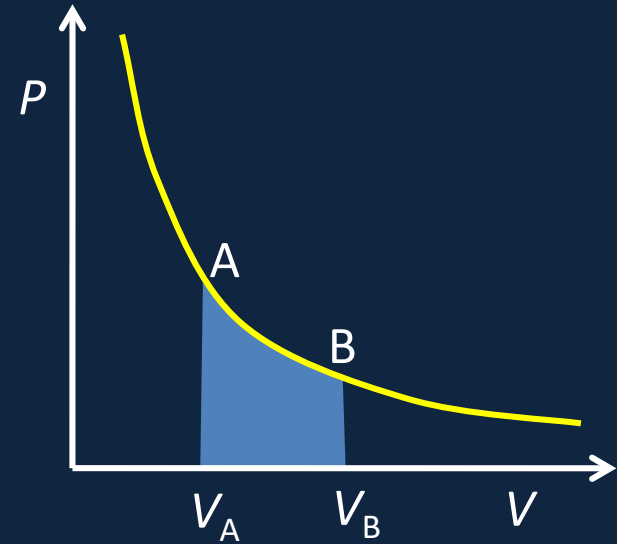
# States of an Ideal Gas

- Note that the work done by the gas in **isothermal** expansion

$$W = \int_{V_A}^{V_B} P dV = \int_{V_A}^{V_B} \frac{nRT}{V} dV = nRT \ln \frac{V_B}{V_A}$$

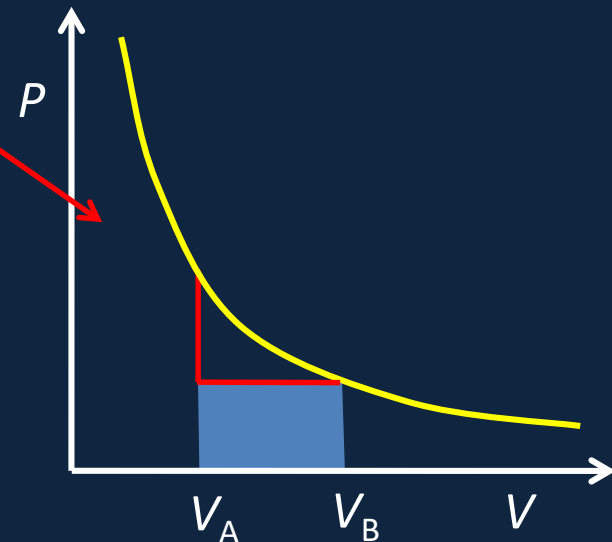
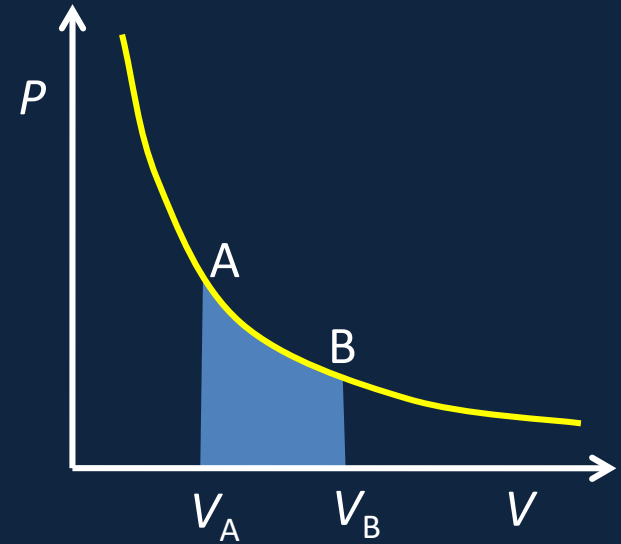
is just the area under the path—  
and in fact this must be true of the  
work done along *any* path.

- The gas clearly does *less* work going from A to B on the **red** path.
- This means less heat is supplied to the gas along the red path!**



# Clicker Question

- What is the *true* heat difference between state A and state B?
- The heat needed to get from state A to state B along the isotherm.
  - The heat supplied going along the red route.
  - The heat needed along a minimal heat transfer route, which may be different from either.
  - The question doesn't make sense.



# Specific Heats of a Mole of Ideal Gas: $C_V$

- If we heat up a gas by  $1^\circ\text{C}$  at constant **pressure**, it will expand and do work, so we **must supply more heat** (to do this work) than if it is heated by  $1^\circ\text{C}$  when kept at constant **volume**.
- Recall that the internal energy of a mole of gas is  $E_{\text{int}} = \frac{3}{2}N_A kT = \frac{3}{2}RT$ .
- Therefore, the heat energy input to raise the temperature  $1^\circ\text{C}$  at constant volume, the constant volume specific heat  $C_V$  is just

$$C_V = \frac{3}{2}R \quad (R = 8.3 \text{ J/mol}\cdot\text{K})$$

# Specific Heats of a Mole of Ideal Gas: $C_p$

- The constant volume specific heat  $C_v$  is just

$$C_v = \frac{3}{2}R \quad (R = 8.3 \text{ J/mol}\cdot\text{K})$$

- For one mole of gas,  $PV = RT$ , so at constant pressure  $P\Delta V = R\Delta T = R$  for a temperature increase of  $1^\circ\text{C}$  (or equivalently 1K).
- This equation also tells us the **work done in expanding at constant pressure**,  $P\Delta V = R$  for one degree—so an extra  $R$  Joules of energy must be supplied above that needed for  $C_v$ ,


$$C_p = C_v + R = \frac{5}{2}R$$

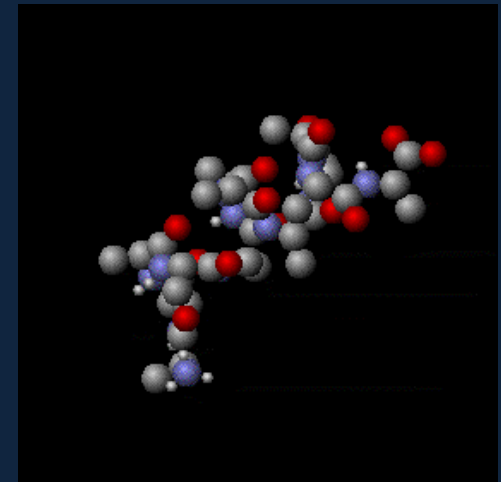
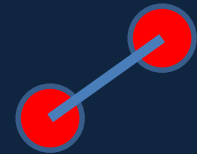


# Molar Specific Heats of Real Gases

- For monatomic gases (He, Ne, Ar) at room temperature, the ideal gas values  $C_V = \frac{3}{2}R$  and  $C_p = C_V + R$  are good to three significant figures.
- **BUT for diatomic gases,  $C_V = (5/2)R$ ,  $C_p = C_V + R$ !**
- Visualize the diatomic molecules as little dumbbells flying around. When two collide, they can set each other **spinning**.
- It can be shown by applying Newton's laws to the collisions that **on average the spinning motion will have equal energy** with the translational motion: this is called the **Equipartition of Energy** .

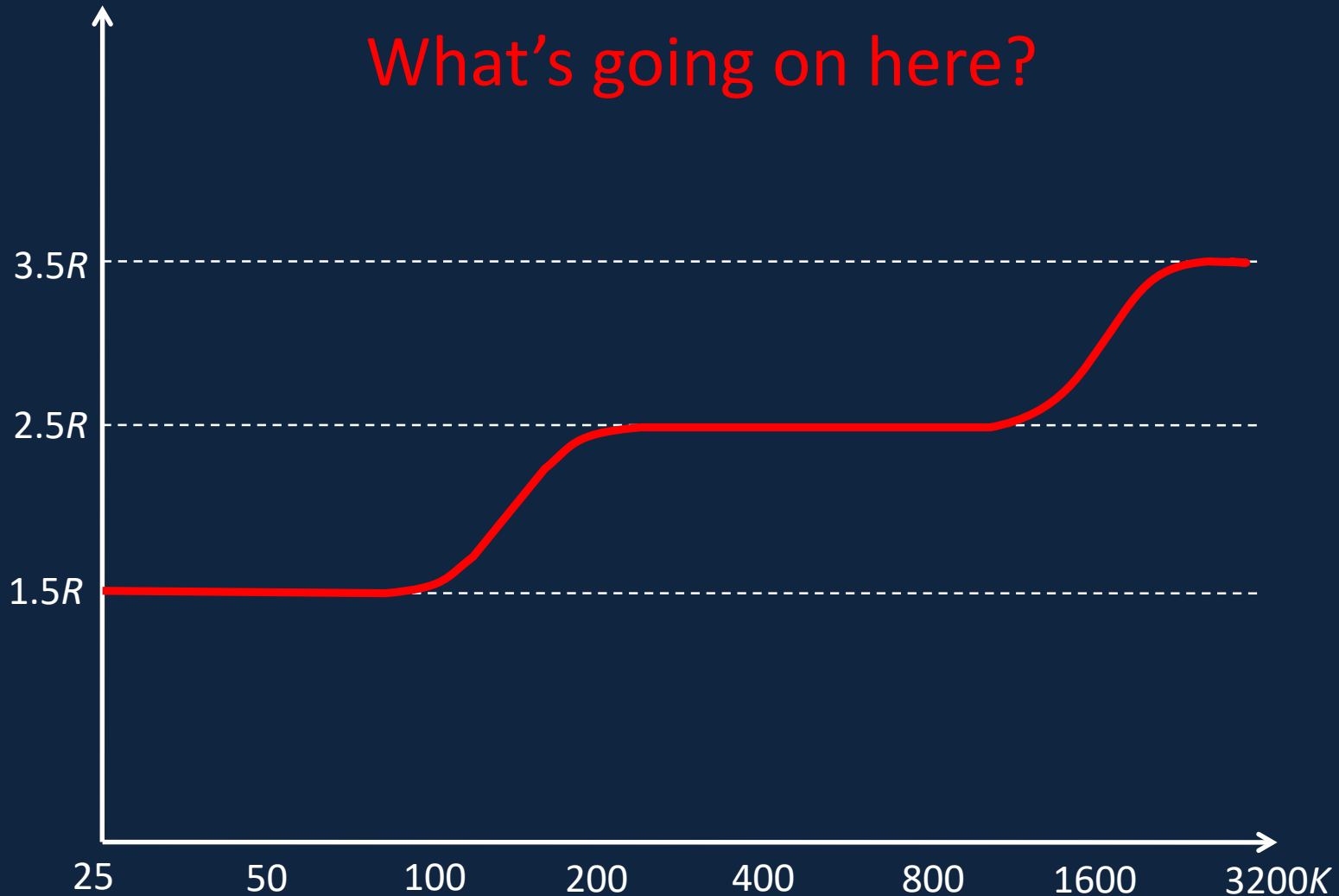
# Equipartition of Energy: Degrees of Freedom

- For the ideal **monatomic** gas, we say the atoms have **three degrees of freedom**, the three different directions  $x, y, z$  and the total kinetic energy is  $\frac{1}{2}m(v_x^2 + v_y^2 + v_z^2)$ . The average atomic  $KE$  is  $\frac{1}{2}kT$  per degree of freedom, for a total  $\frac{3}{2}kT$ .
- The **diatomic** gas has specific heat  $2.5kT$ : evidently there are **two more** degrees of freedom: obviously rotation about axes perpendicular to the line of the molecule.
- Bigger molecules have many more possibilities, like vibrational energy. 



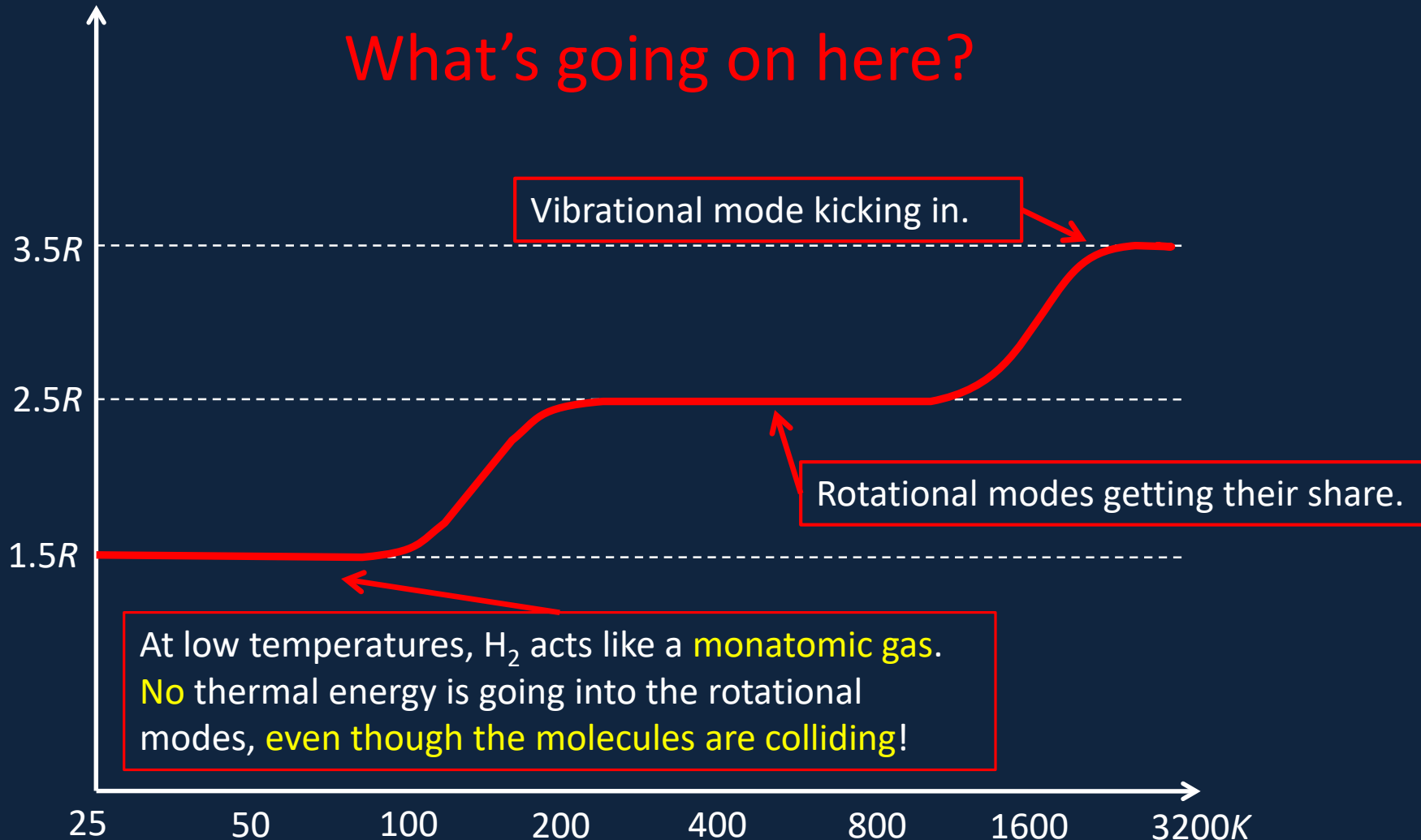
# An Equipartition Puzzle: Specific Heat of $H_2$ as a Function of $T$

What's going on here?



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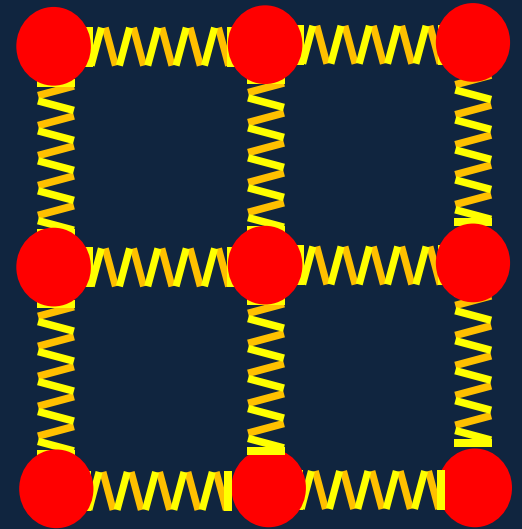


# Puzzle Answered: the Quantum Theory

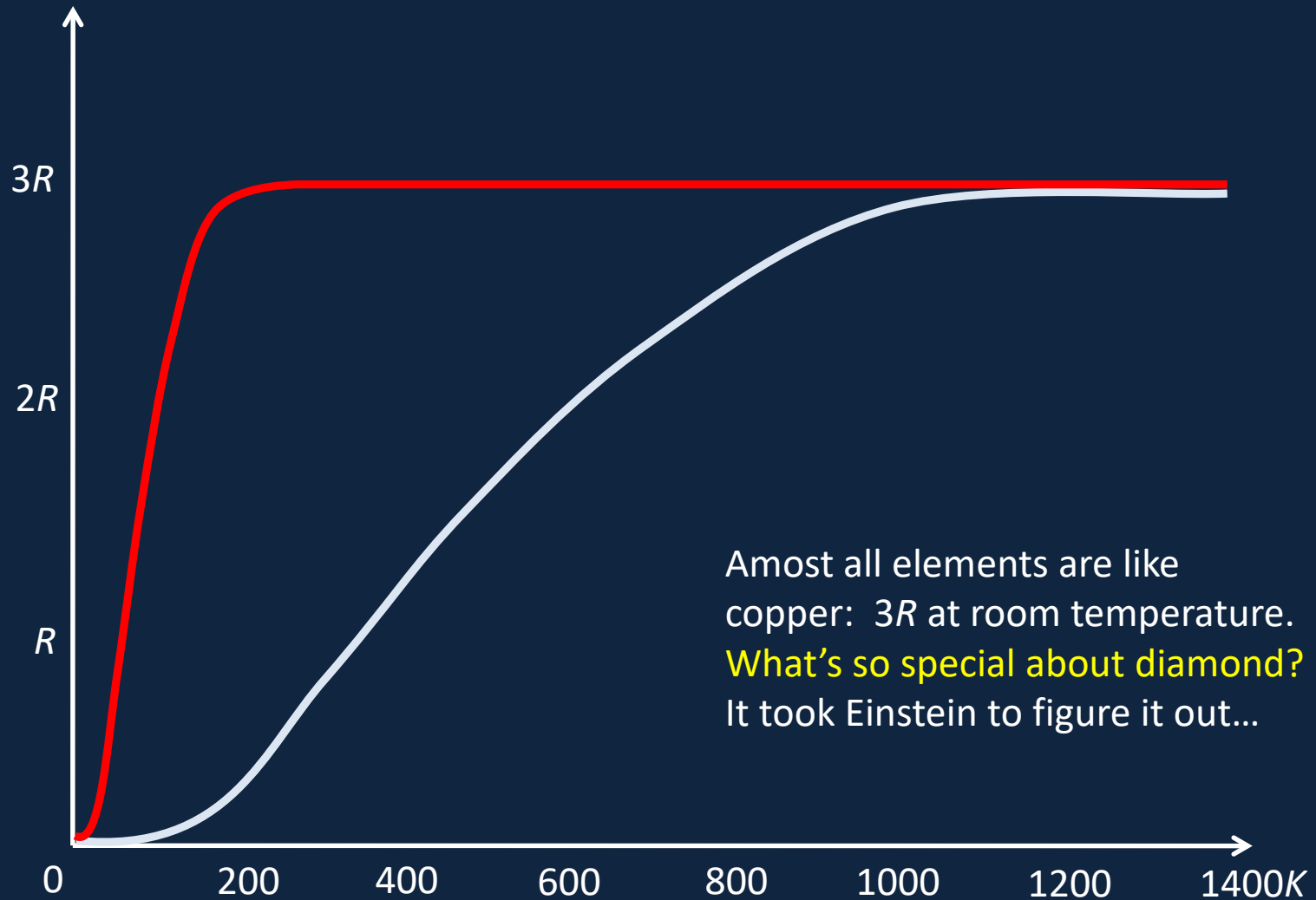
- Newton's Laws don't work here. This temperature dependence of the specific heat of real H<sub>2</sub> gas can *only* be understood with **quantum mechanics!**
- It turns out that the **angular momentum of a spinning object can only have values which are whole numbers times  $\hbar$** , where  $\hbar$  is Planck's constant/ $2\pi$ ,  $\hbar = 1.06 \times 10^{-34}$  J·sec.
- The H<sub>2</sub> molecule has such a tiny moment of inertia it takes quite a kick to spin it fast enough for the minimum allowed angular momentum—so it doesn't get to spin at low temperatures.

# Molar Specific Heat of Solids

- Many simple solids, such as elements, can be pictured as a lattice of balls connected by springs, a 3-D version of this: 
- Each atom acts like an oscillator with three degrees of freedom, each degree has both  $KE$  and  $PE$ , suggesting a molar specific heat of  $3R$ .
- This is just the Dulong Petit value, and works well for many elements except at low temperatures ...



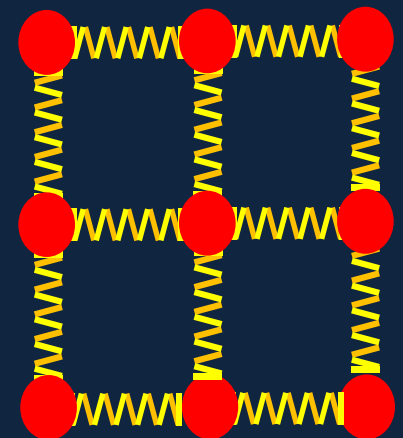
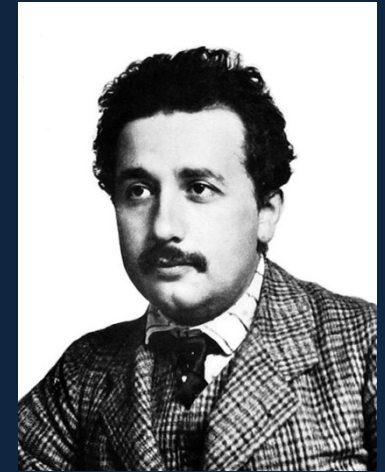
# Molar Specific Heats of Copper and Diamond



Almost all elements are like copper:  $3R$  at room temperature.  
**What's so special about diamond?**  
It took Einstein to figure it out...

# Einstein Solves the Puzzle

- Einstein assumed each atom was basically a 3D mass-on-a-spring oscillator.
- The difference with **diamond** is that its masses are quite small (carbon) and its springs are very strong—diamond is *hard*! This means the oscillators have **very high frequency  $\omega$** .
- **Einstein suggested** that like the rotators, **these oscillators could only absorb energy in chunks**, called **quanta**, and one chunk was  $\hbar\omega$  – the same  $\hbar$  as the rotators.
- That means higher frequency diamond oscillators could only absorb energy in bigger chunks—so they **froze out** at low temperatures.
- Copper's oscillators freeze out too—but at lower  $T$ .





# Clicker Question

- At the liquid nitrogen boiling temperature (77K) the molar specific heat of copper is about half its room temperature value.
- What would you expect the molar specific heat of lead to be at that temperature?
  - A. Less than copper
  - B. The same as copper
  - C. Higher than copper.

Hint: think of the atom oscillators. Is lead hard? Is it heavy?

# Adiabatic Expansion of an Ideal Gas

- “Adiabatic” is Greek for “nothing gets through”—here it means no heat gets into or out of the gas. Therefore, for one mole,

$$dE_{\text{int}} = C_V dT = -PdV$$

- From  $PV = RT$ ,  $RdT = PdV + VdP$ , putting that  $dT$  in the equation, and defining  $\gamma = C_p/C_V$ , we can show that  $VdP + \gamma PdV = 0$ , which integrates to

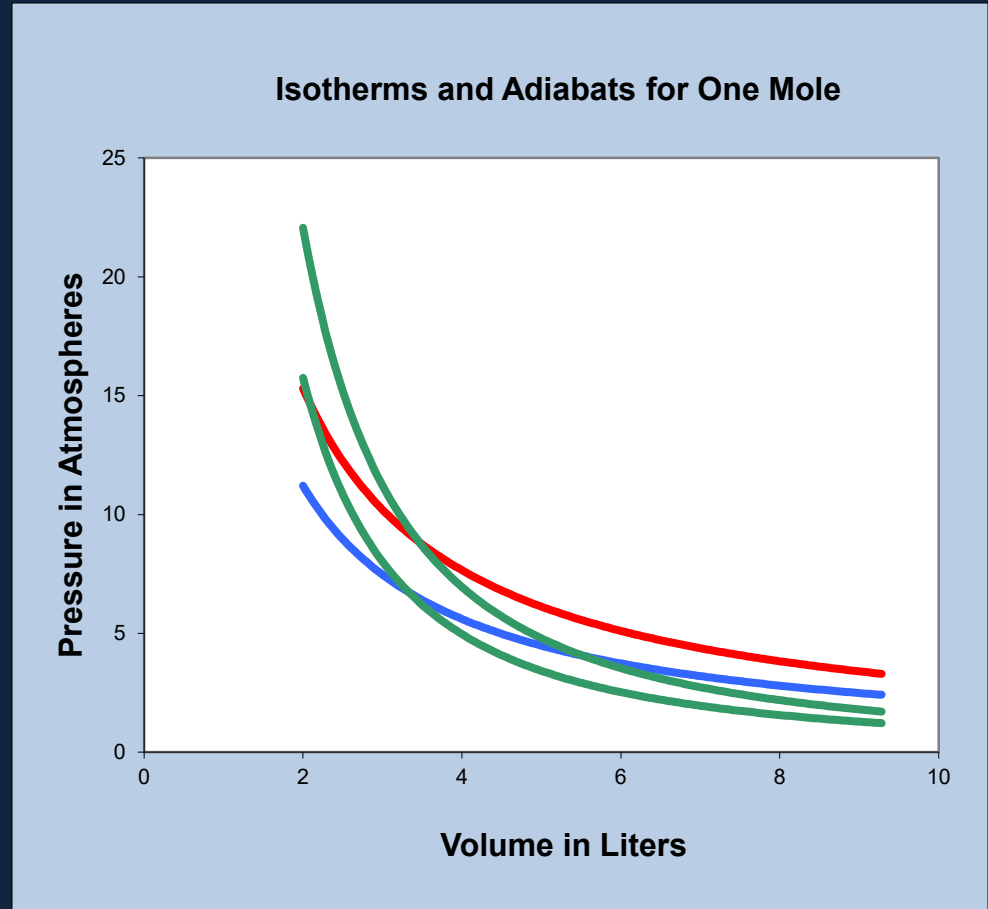
$$PV^\gamma = \text{constant.}$$

# Clicker Question

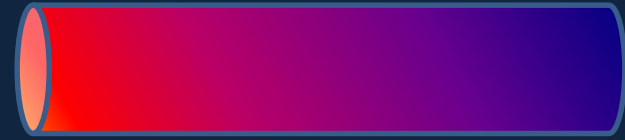
- Two identical cylinders contain the same volume  $V$  of ideal gas, initially at the same temperature and pressure.
- Gas A is then compressed adiabatically to  $\frac{1}{2}V$ , and gas B is compressed isothermally to  $\frac{1}{2}V$ .
- Which is now at the greater pressure?
  - A.
  - B.
  - C. They're equal.

# Isotherms and Adiabats

- **Adiabats** are steeper than **isotherms** because work done compressing the gas along the adiabat all goes into internal energy—the gas heats up. Compressing along the isotherm, the gas continuously sheds heat.

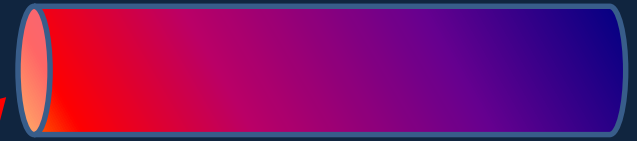


# Heat Conduction



- Heat conduction through solids acts just like a fluid flow—that’s why the caloric theory worked so well. The flow of heat down a rod is proportional to the temperature gradient (like a river flowing downhill), proportional to the cross-section area of the rod (like water in a pipe) and varies from material to material depending on the “thermal conductivity”  $k$ , a property of the material.

# Heat Flow down a Rod



- For a rod of material with thermal conductivity  $k$ , length  $\ell$  and cross-section area  $A$ , the heat flow  $\Delta Q$  in time  $\Delta t$  is given by:

$$\frac{\Delta Q}{\Delta t} = kA \frac{T_1 - T_2}{\ell}$$

or differentially

$$\frac{dQ}{dt} = -kA \frac{dT}{dx}$$

# Microscopic Picture of Heat Conduction

- If one end of a nonmetallic rod is heated, the atoms near that end vibrate more vigorously and emit tiny sound waves, called phonons, that travel down the rod. These go at the speed of sound, but are easily scattered by impurities or lattice defects, so they actually diffuse down the rod, like molecules in a gas, and in comparable times—they move at similar speeds to molecules and in many solids have mean free paths of tens or hundreds of atomic spacings.

# Heat Conduction in Metals

- Metals are shiny materials that conduct electricity well. Both these properties are due to the presence of large numbers of “**free electrons**”—electrons not bound to individual atoms, but free to move through the material. (We’ll understand why that makes them shiny next semester.)
- The **electrons are excellent conductors of heat**—they move very fast and have long mean free paths.
- **Metals typically conduct heat a hundred times better than nonmetals.**



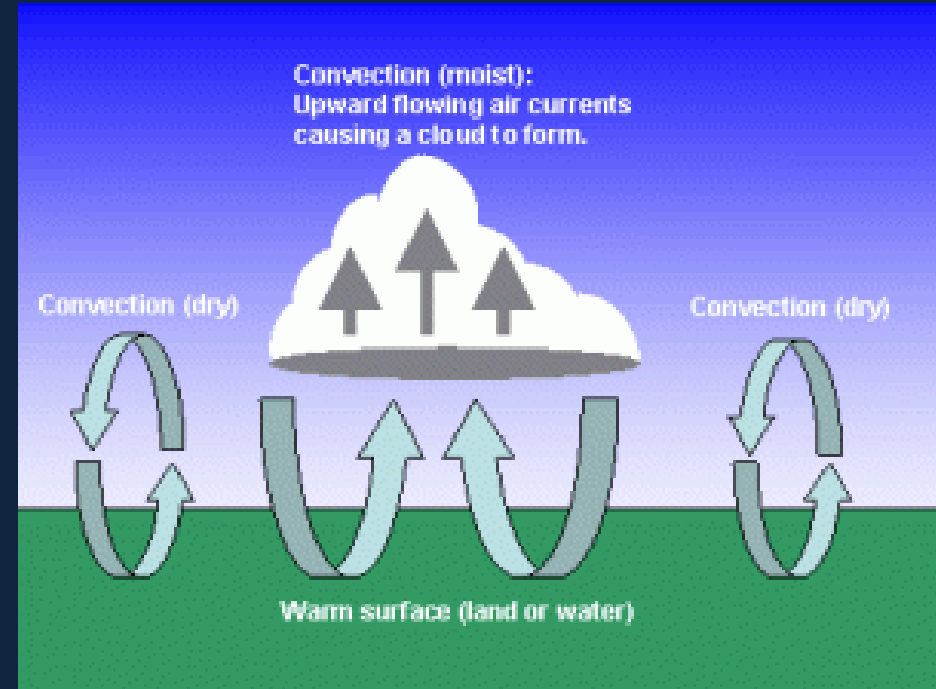
# Heat Insulators

- Heat insulators are solids that are in fact mostly air—rockwall insulation → has a density about 12% that of water, it's just full of tiny holes filled with air, and air is a poor *conductor* of heat—heat moves through the atmosphere by convection and radiation. These holes are too small for convection currents to get set up.
- Goosedown and polyurethane are even better heat insulators, but lack structural strength.



# Convection

- If a fluid is heated from below, like the atmosphere over hot ground, the less dense air moves upwards. If it contains moisture, this may eventually condense out as the temperature drops below the dew point, forming a cloud.
- Convection works *upside down* to cool a lake from the surface downwards as winter begins—**BUT stops at 4°C**—below that temperature the water's density *decreases*, and the cold stays on top.



# Radiation

- All bodies radiate thermal energy: this radiation is electromagnetic waves generated by the motion of electric charges oscillating with the heat vibrations in the solid. (This will be discussed much more next semester.)
- The intensity of radiation from a surface, in **watts/sq m**, depends on the surface material: it's proportional to an experimentally determined **coefficient of emissivity**, called  $e$  or  $\epsilon$ , varying from 0 to 1, 1 being the best possible radiator.
- $\epsilon = 1$  is called a **perfect black body**.

# Solar Radiation

- The intensity of black body radiation varies with absolute temperature,

$$I = \sigma T^4 \text{ watts/m}^2$$

where Stefan's constant  $\sigma = 5.67 \times 10^{-8} \text{ watts/m}^2 \cdot \text{K}^4$ .

- The sun, at 5780K, radiates about **60 megawatts** per square meter of surface. This reaches Earth at an intensity of **1.35kW/sq m** (above the atmosphere), this is called the **solar constant**.

# Radiation Equilibrium

- You are currently radiating energy proportional to the **fourth power of your temperature** in kelvins. But so is everyone else, and the walls, etc., so **you are also receiving radiant energy**.
- If an object is left in a constant temperature room, it reaches that temperature and stays there. **This means its ability to absorb radiant energy must exactly equal its emissivity**.
- Before reaching equilibrium, the energy transfer rate per sq m of surface is  $\varepsilon \sigma (T_{\text{obj}}^4 - T_{\text{room}}^4)$ .

# EARTH'S ENERGY BUDGET

