

Lecture 4

1st Law of Thermodynamics

(sections 19-4 to 19-9)

19-4 Calorimetry

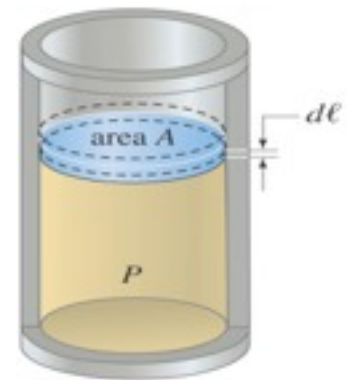
19-5 Latent Heat

19-6 The 1st Law of Thermodynamics

19-7 Gas: Calculating the Work

19-8 Molar Specific Heats

19-9 Adiabatic Gas Expansion



19-4 Calorimetry

Definitions:

Closed system: no mass enters or leaves, but energy may be exchanged

Open system: mass may transfer as well

Isolated system: closed system in which no energy in any form is transferred

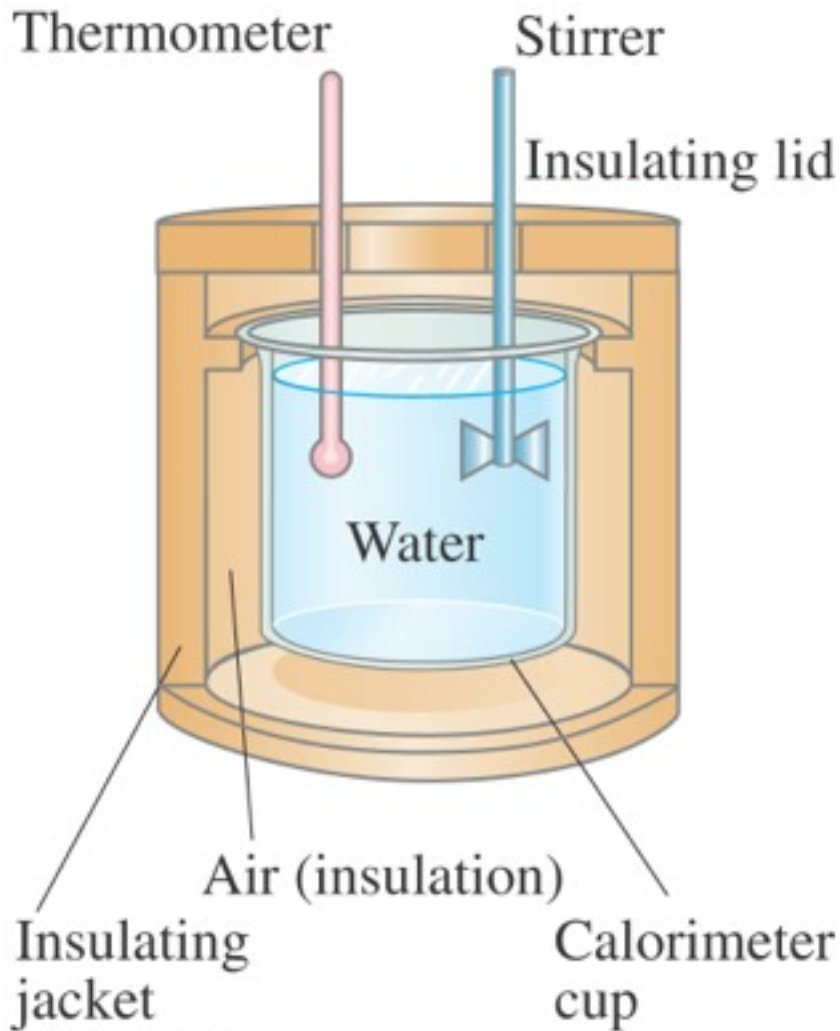
For an isolated system,

energy out of one part = energy into another part,

or:

heat lost = heat gained.

19-4 Calorimetry—Solving Problems



The instrument to the left is a **calorimeter**, which makes **quantitative measurements of heat exchange**. A sample of mass m_{sample} is heated to a well-measured high temperature T_{sample} and plunged into the water, and the **equilibrium temperature** is measured. This gives the **specific heat of the sample**.

heat lost = heat gained :

$$C_{\text{sample}} m_{\text{sample}} (T_{\text{sample}} - T_{\text{eq}}) = C_{\text{water}} m_{\text{water}} (T_{\text{eq}} - T_{\text{initial}}) + C_{\text{calorim}} m_{\text{calorim}} (T_{\text{eq}} - T_{\text{initial}})$$

The only unknown is C_{sample} .

19-5 Latent Heat

The **total** heat required for a phase change depends on the **total mass** and the **latent heat**:

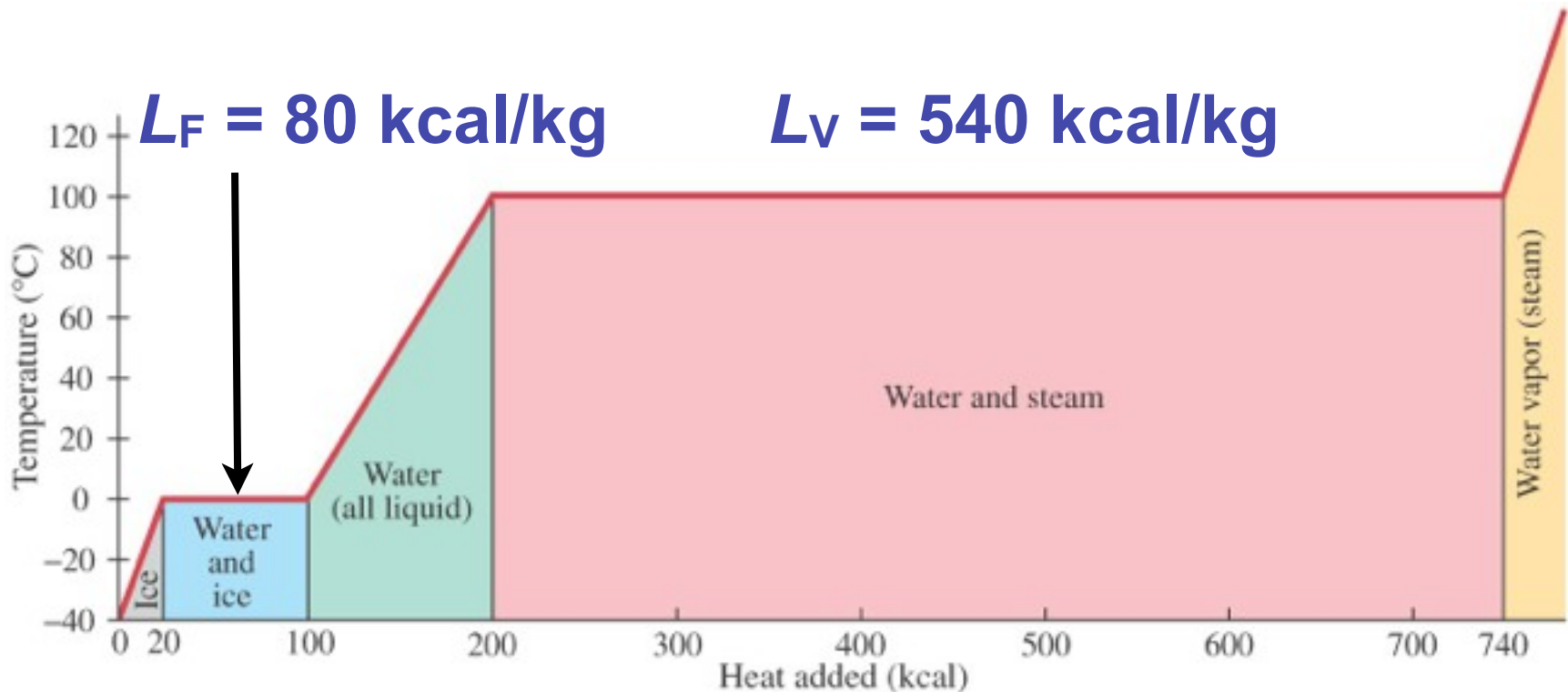
$$Q = mL.$$

The **latent heat of vaporization** is relevant for **evaporation as well as boiling**. The heat of vaporization of water rises slightly as the temperature decreases.

On a **molecular level**, the heat added during a change of state does not go to increasing the **kinetic energy** of individual molecules, but rather to **breaking the close bonds** between them so the **next phase** can occur.

19-5 Latent Heat

Energy is required for a material to change phase, even though its temperature is not changing. The diagram shows the latent heats of fusion L_F and vaporization L_V for water.



19-5 Latent Heat

Heat of fusion, L_F : heat required to change 1.0 kg of material from solid to liquid

Heat of vaporization, L_V : heat required to change 1.0 kg of material from liquid to vapor

TABLE 19–2 Latent Heats (at 1 atm)

Substance	Melting Point (°C)	Heat of Fusion		Boiling Point (°C)	Heat of Vaporization	
		kcal/kg†	kJ/kg		kcal/kg†	kJ/kg
Oxygen	−218.8	3.3	14	−183	51	210
Nitrogen	−210.0	6.1	26	−195.8	48	200
Ethyl alcohol	−114	25	104	78	204	850
Ammonia	−77.8	8.0	33	−33.4	33	137
Water	0	79.7	333	100	539	2260
Lead	327	5.9	25	1750	208	870
Silver	961	21	88	2193	558	2300
Iron	1808	69.1	289	3023	1520	6340
Tungsten	3410	44	184	5900	1150	4800

†Numerical values in kcal/kg are the same in cal/g.

To cool a hot drink, would it better to add an ice cube at 0 °C or an identical mass of water at 0 °C?

- A. An ice cube
- B. The water
- C. It makes no difference.

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• **A. An ice cube**

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The ice cube requires an extra 80 cal/g latent heat to melt.

Which is usually worse – a hot water burn or a steam burn?

- A. A hot water burn, because the water makes better contact with the skin.
- B. A steam burn, because the latent heat of the steam is released when the steam condenses on the skin.

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Two balls of putty collide and stick together. Which of the following statement is not true?

- A. Total momentum is conserved.
- B. Total mechanical energy is conserved.
- C. Total energy is conserved.
- D. The internal energy of the putty balls increases.
- E. They are all true.

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A car slows down as a result of air resistance. Which is true?

- A. The car's kinetic energy decreases.
- B. Heat is generated.
- C. The energy of the car/road/air system is constant.
- D. all of the above
- E. none of the above

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19-6 The First Law of Thermodynamics

The change in internal energy of a closed system will be equal to the energy added to the system minus the work done by the system on its surroundings.

$$\Delta E_{\text{int}} = Q - W$$

This is the law of conservation of energy, written in a form useful to systems involving heat transfer.

2500 J of heat is added to a system, and 1800 J of work is done on the system. What is the change in internal energy of the system?

A. +700 J

B. -700 J

C. +4300 J

D. -4300 J

E. none of the above

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19-6 The First Law of Thermodynamics

The first law

$$\Delta E_{\text{int}} = Q - W$$

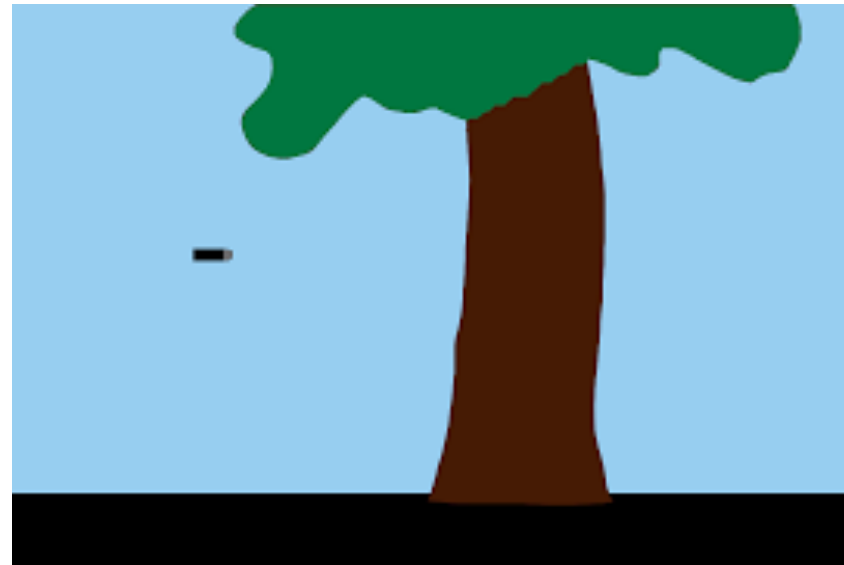
can be extended to include changes in
mechanical energy =

kinetic energy K + potential energy U :

$$\Delta K + \Delta U + \Delta E_{\text{int}} = Q - W.$$

A 3.0-g bullet traveling at a speed of 400 m/s enters a tree and exits the other side with a speed of 200 m/s. Where did the bullet's lost kinetic energy go, and how much energy was transferred? (This requires calculation.)

- A. Potential energy, 1.80×10^5 J**
- B. Potential energy, 180 J**
- C. Internal energy, 1.80×10^5 J**
- D. Internal energy, 180 J**
- E. none of the above**



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D. Internal energy, 180 J

E. none of the above

$$v_i = 400 \text{ m/s} \quad v_f = 200 \text{ m/s}$$

$$KE_i - KE_f = \frac{1}{2} m (v_i^2 - v_f^2)$$

$$= \frac{1}{2} 3 \times 10^{-3} (16 - 4) \times 10^4 \text{ J}$$

$$= 180 \text{ J}$$

was transferred to the tree as heat

Which of these statements is true?

- A. If heat flows into a substance, its temperature must rise.
- B. If the temperature of a substance rises, heat must have flowed into it.
- C. both A and B
- D. neither A nor B

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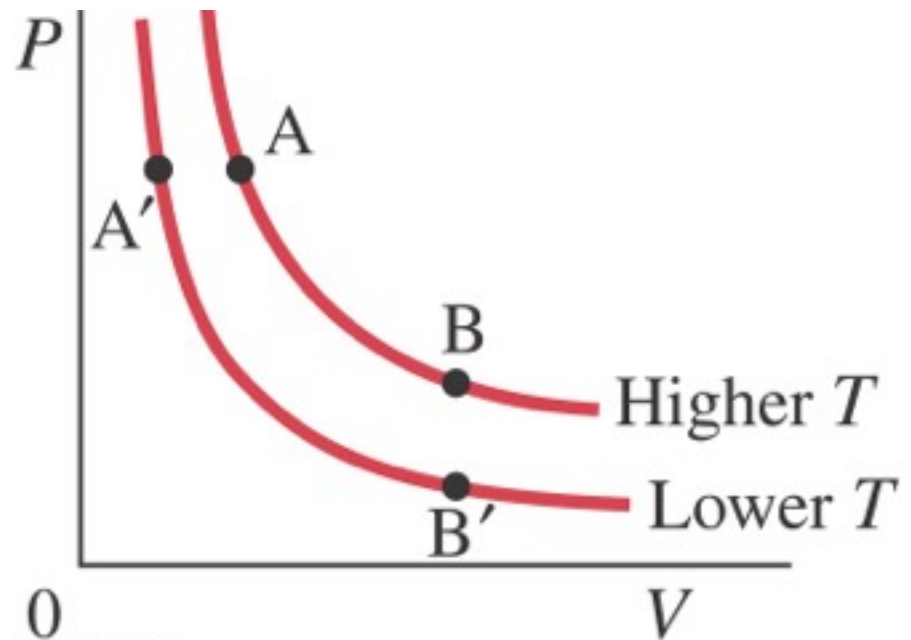
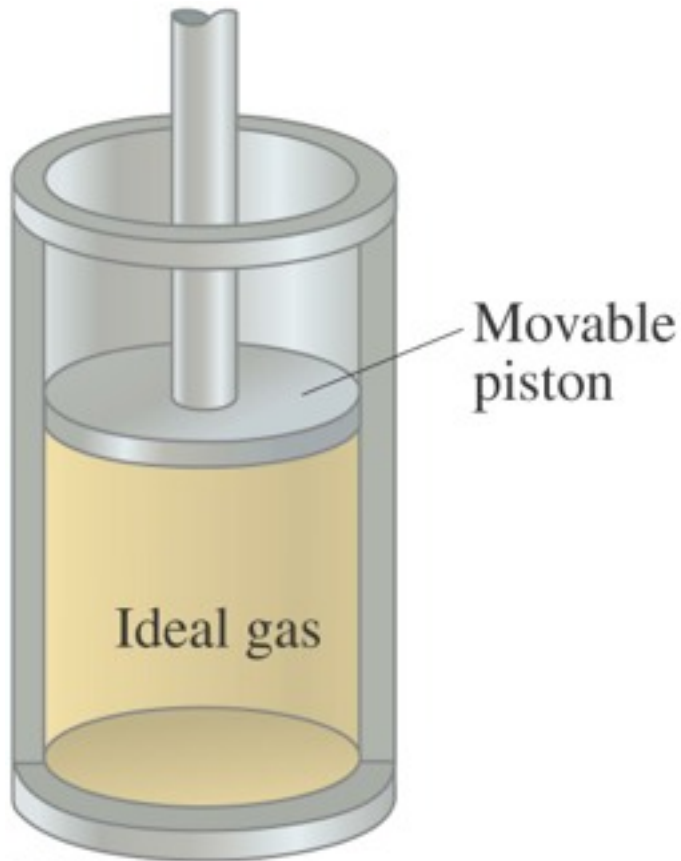
$$\Delta E_{\text{int}} = Q - W$$

Not A, since all the heat could be converted to work.

Not B, since work could have been done on it.

19-7 The First Law of Thermodynamics Applied; Calculating the Work

An **isothermal** process is one in which the temperature does not change.



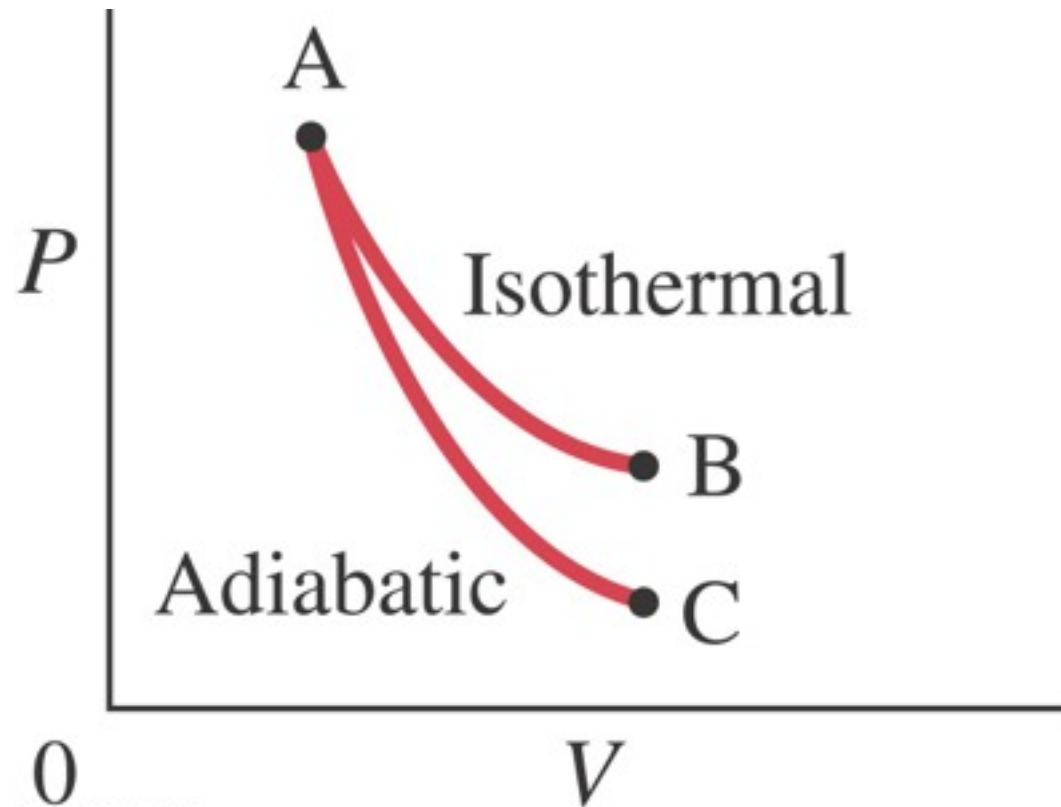
19-7 The First Law of Thermodynamics Applied; Calculating the Work

In order for an isothermal process to take place, we assume the system is in contact with a heat reservoir.

In general, in introductory thermodynamics we assume that the system remains in equilibrium throughout all processes.

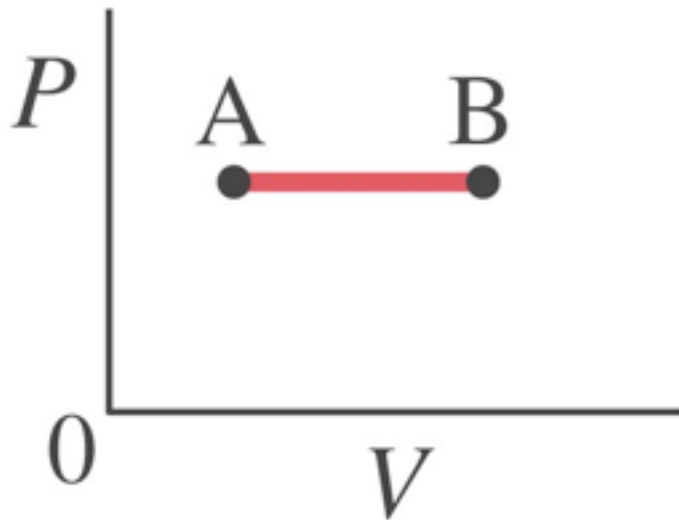
19-7 The First Law of Thermodynamics Applied; Calculating the Work

An **adiabatic** process is one in which there is no heat flow into or out of the system.

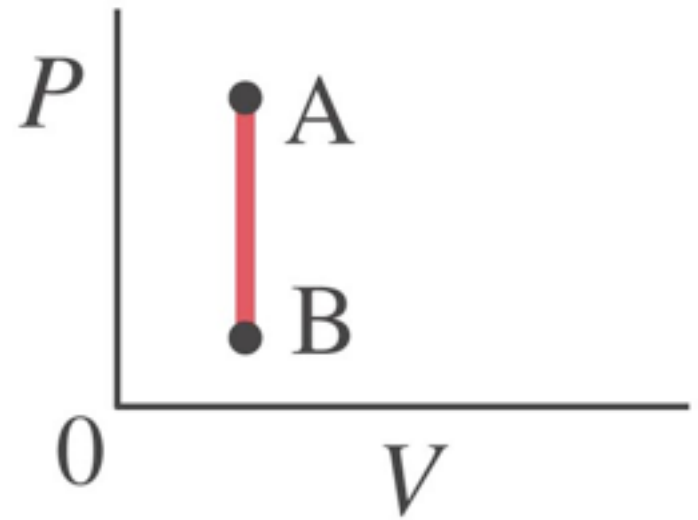


19-7 The First Law of Thermodynamics Applied; Calculating the Work

An **isobaric** process (a) occurs at constant pressure; an **isovolumetric** one (b) occurs at constant volume.

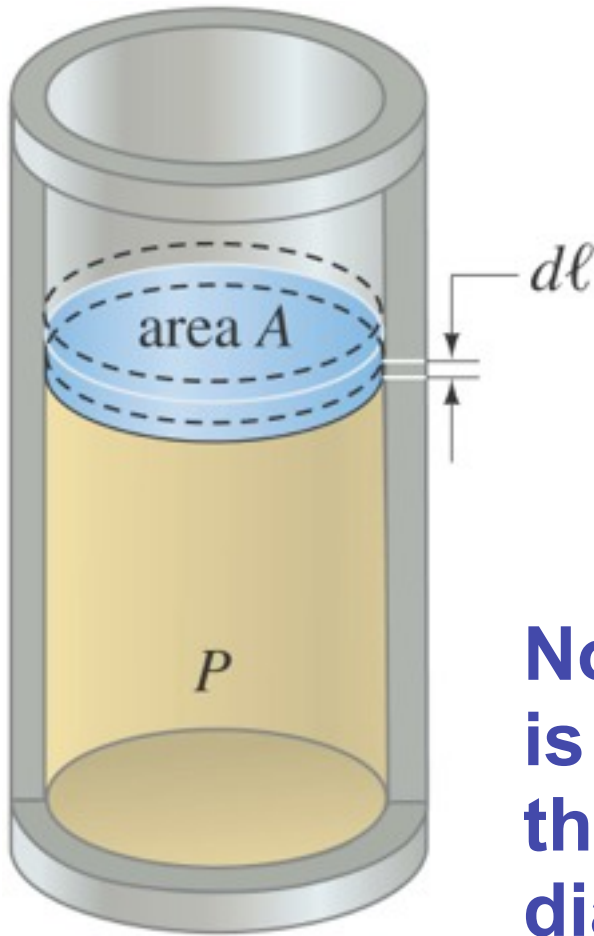


Isobaric



Isovolumetric

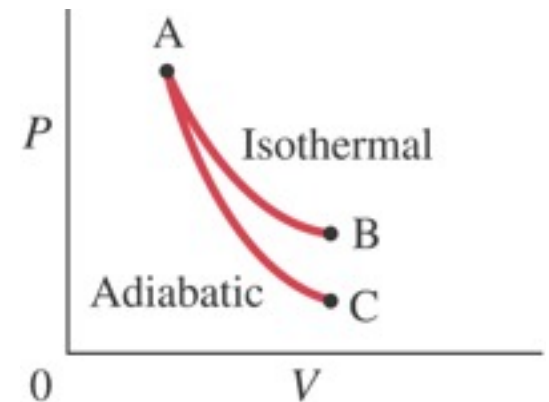
19-7 The First Law of Thermodynamics Applied; Calculating the Work



The work done in moving a piston by an infinitesimal displacement is:

$$dW = \vec{\mathbf{F}} \cdot d\vec{\ell} = PA d\ell = P dV.$$

Note: $W = \int P dV$ is the area under the curve on a P - V diagram.



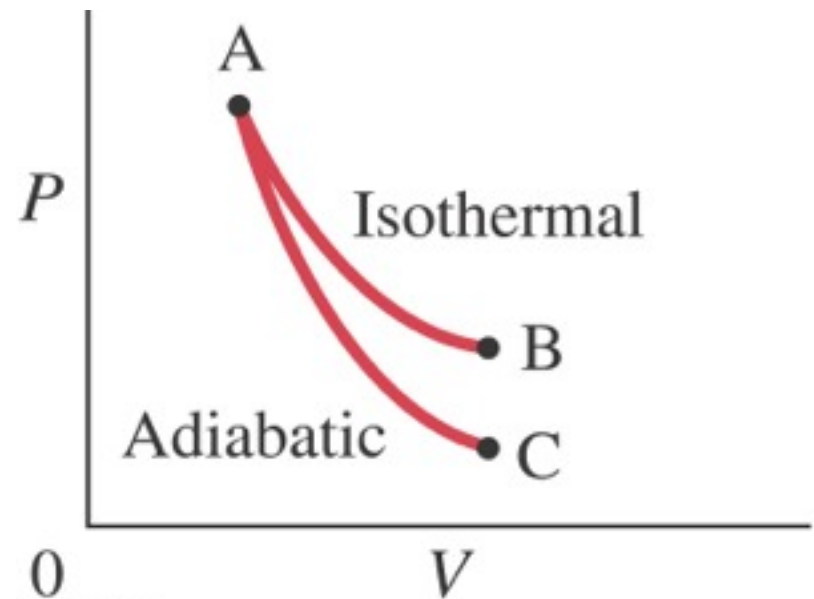
19-7 The First Law of Thermodynamics Applied; Calculating the Work

Reproduced here is the PV diagram for a gas expanding in two ways, isothermally and adiabatically. The initial volume V_A was the same in each case, and the final volumes were the same ($V_B = V_C$). In which process was more work done by the gas,

Isothermal?

or

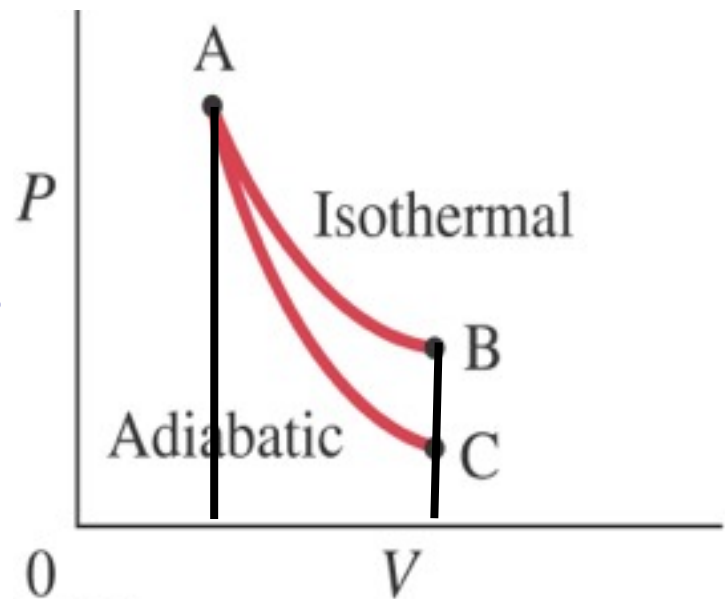
Adiabatic?



19-7 The First Law of Thermodynamics Applied; Calculating the Work

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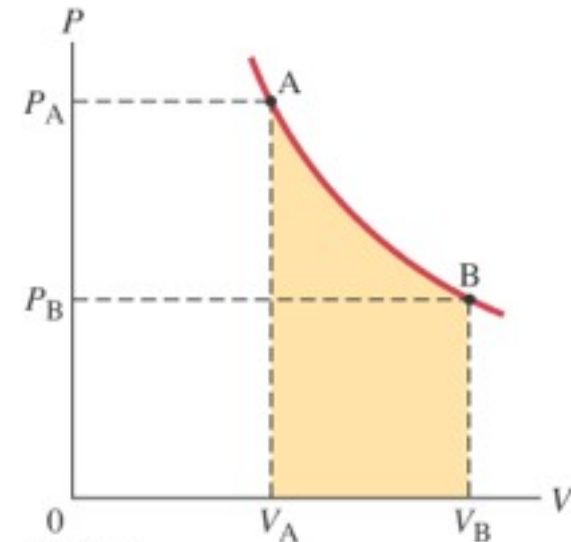
Answer: Work $W = \int PdV$ = the area under the curve. The area under curve AB is greater than under AC, so more work is done in the **isothermal** process.



19-7 The First Law of Thermodynamics Applied; Calculating the Work

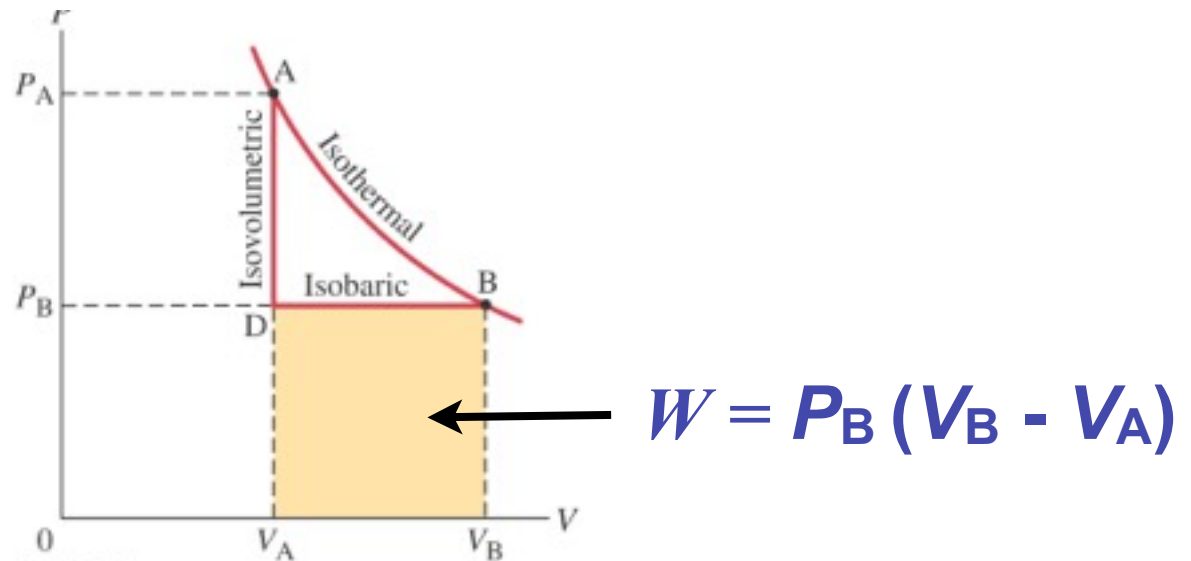
For an ideal gas expanding isothermally, $P = nRT/V$. Integrating to find the work done in taking the gas from point A to point B gives:

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



19-7 The First Law of Thermodynamics Applied; Calculating the Work

A different path takes the gas first from A to D in an isovolumetric process; because the volume does not change, no work is done: $P\Delta V = 0$. Then the gas goes from D to B at constant pressure; with constant pressure the integration is trivial: $W = P_B (V_B - V_A)$.



19-7 The First Law of Thermodynamics Applied; Calculating the Work

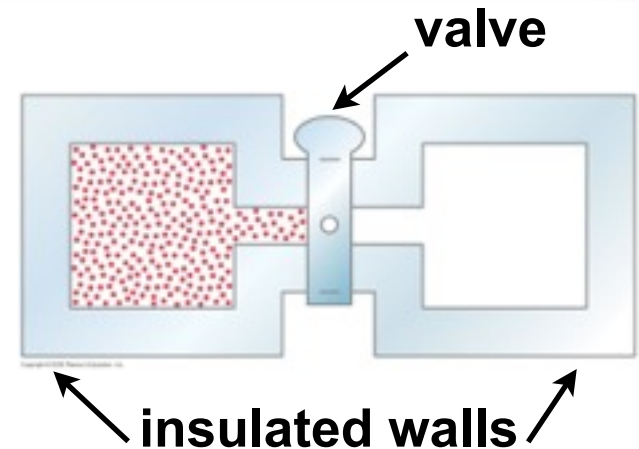
$$\Delta E_{\text{int}} = Q - W$$

The following is a simple summary of the various thermodynamic gas processes:

TABLE 19–3 Simple Thermodynamic Processes and the First Law

Process	What is constant:	The first law predicts:
Isothermal	$T = \text{constant}$	$\Delta T = 0$ makes $\Delta E_{\text{int}} = 0$, so $Q = W$
Isobaric	$P = \text{constant}$	$Q = \Delta E_{\text{int}} + W = \Delta E_{\text{int}} + P \Delta V$
Isovolumetric	$V = \text{constant}$	$\Delta V = 0$ makes $W = 0$, so $Q = \Delta E_{\text{int}}$
Adiabatic	$Q = 0$	$\Delta E_{\text{int}} = -W$

Free expansion is an adiabatic process: when the valve is opened, the gas expands with no change in its internal energy: $W = 0$, $Q = 0$, so $\Delta E_{\text{int}} = 0 \Rightarrow$ for an ideal gas $\Delta T = 0$.



19-8 Molar Specific Heats for Gases, and the Equipartition of Energy

For gases, the molar specific heat depends on the process—the isobaric (constant pressure) molar specific heat C_P is different from the isovolumetric one C_V .

$$Q = nC_V\Delta T$$

$$Q = nC_P\Delta T$$



n = number of moles

19-8 Molar Specific Heats for Gases, and the Equipartition of Energy

In this table, we see that the specific heats for gases with the same number of molecules are almost the same, and that the difference $C_P - C_V$ is almost exactly equal to 2 cal/mol-K in all cases.

Gas	Specific heats (kcal/kg · K)		Molar specific heats (cal/mol · K)		$C_P - C_V$ (cal/mol · K)	$\gamma = \frac{C_P}{C_V}$
	c_V	c_P	C_V	C_P		
Monatomic						
He	0.75	1.15	2.98	4.97	1.99	1.67
Ne	0.148	0.246	2.98	4.97	1.99	1.67
Diatomic						
N ₂	0.177	0.248	4.96	6.95	1.99	1.40
O ₂	0.155	0.218	5.03	7.03	2.00	1.40
Triatomic						
CO ₂	0.153	0.199	6.80	8.83	2.03	1.30
H ₂ O (100°C)	0.350	0.482	6.20	8.20	2.00	1.32

19-8 Molar Specific Heats for Gases, and the Equipartition of Energy

For a gas in a constant-volume process, no work is done, so $Q_V = \Delta E_{\text{int}} = C_V \Delta T$.

For a gas at constant pressure, $Q_P = \Delta E_{\text{int}} + P\Delta V$.

Comparing these two processes for a monatomic gas when ΔT is the same gives $Q_P = nC_P\Delta T = nC_V\Delta T + nR\Delta T$, so dividing by $n\Delta T$ gives

$$C_P - C_V = R,$$

which is consistent with the measured values (note that $R = 1.99 \text{ cal/mol-K}$).

19-8 Molar Specific Heats for Gases, and the Equipartition of Energy

In addition, since for a monatomic gas

$$\Delta E_{\text{int}} = \frac{3}{2} nR \Delta T = nC_V \Delta T,$$

we expect that

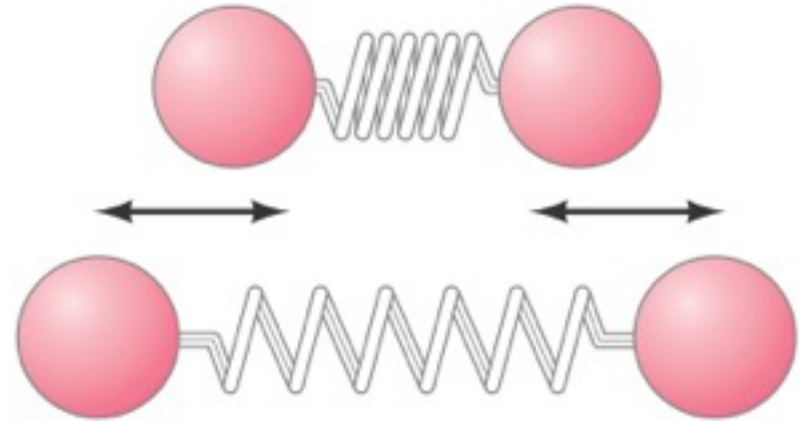
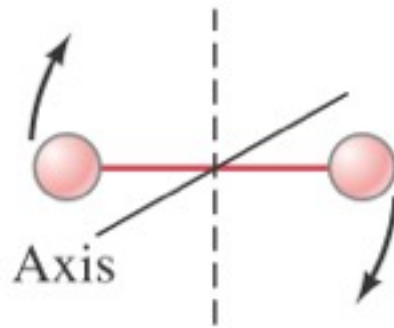
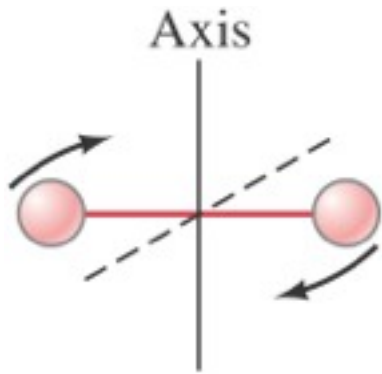
$$C_V = \frac{3}{2} R.$$

This is also in agreement with measurements for monatomic gases.

Gas	Specific heats (kcal/kg · K)		Molar specific heats (cal/mol · K)		$C_P - C_V$ (cal/mol · K)	$\gamma = \frac{C_P}{C_V}$
	c_V	c_P	C_V	C_P		
Monatomic						
He	0.75	1.15	2.98	4.97	1.99	1.67
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Diatomic						

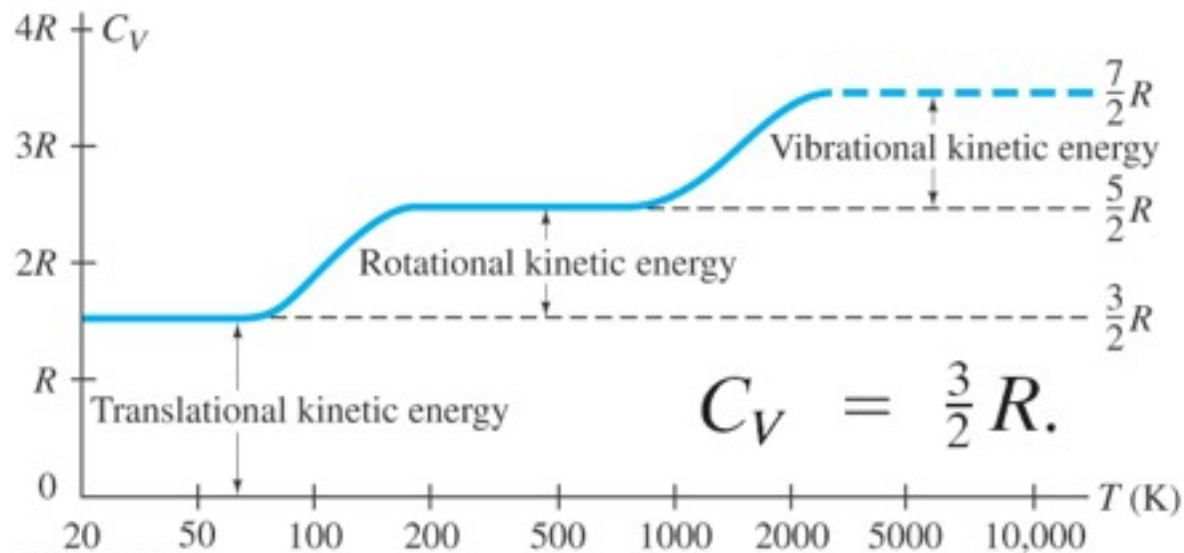
19-8 Molar Specific Heats for Gases, and the Equipartition of Energy

For a gas consisting of more complex molecules (diatomic or more), the molar specific heats increase. This is due to the extra forms of internal energy that are possible (rotational, vibrational).



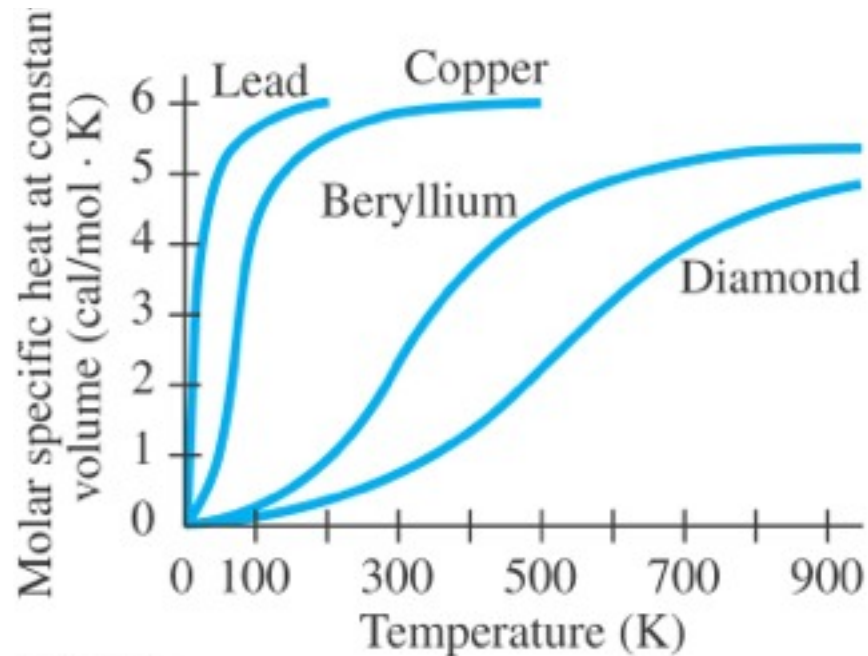
19-8 Molar Specific Heats for Gases, and the Equipartition of Energy

Each mode of vibration or rotation is called a **degree of freedom**. The equipartition theorem states that the total internal energy is shared equally among the active degrees of freedom, each accounting for $\frac{1}{2} kT$. The actual measurements show a more complicated situation.



19-8 Molar Specific Heats for Gases, and the Equipartition of Energy

For solids at high temperatures, C_V is approximately $3R$, corresponding to six degrees of freedom (three kinetic energy and three vibrational potential energy) for each atom.



19-9 Adiabatic Expansion of a Gas

For an adiabatic expansion, $dE_{\text{int}} = -PdV$, since there is no heat transfer. From the relationship between the change in internal energy and the molar heat capacity, $dE_{\text{int}} = nC_V dT$.

From the ideal gas law, $PdV + VdP = nRdT$.

Combining and rearranging* gives $(C_P/C_V)PdV + VdP = 0$, or $\gamma dV/V + dP/P = 0$, hence $PV^\gamma = \text{const}$.

Recall that we defined $\gamma = C_P/C_V$. *In more detail:

$dE_{\text{int}} = -PdV = nC_V dT = nC_V (PdV + VdP)/nR$. Thus

$-RPdV = C_V (PdV + VdP)$, $(\underbrace{C_V + R}_{= C_P}) PdV + C_V VdP = 0$,
and divide by $C_V PV$