

Lecture 39

Thermodynamic processes.

Heat capacities.

Types of processes

Reversible

- must be slow (quasistatic: system has time to go to equilibrium after each change)
- system is in equilibrium at all points along the process
- corresponds to a line in pV diagram
- can be run in reverse

Irreversible

- often fast (but not always)
- is not a line in pV diagram (you can only mark initial and final states)
- cannot run in reverse
eg. explosion



Basic thermodynamic processes

- **Isobaric:** Constant p

$$W = p\Delta V$$

- **Isochoric:** Constant V

$$W = 0$$

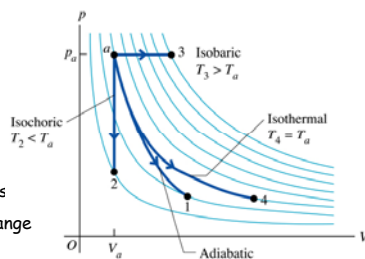
- **Isothermal:** Constant T

$$\Delta U = 0 \text{ for ideal gases}$$

- **Adiabatic:** No heat exchange

$$Q = 0$$

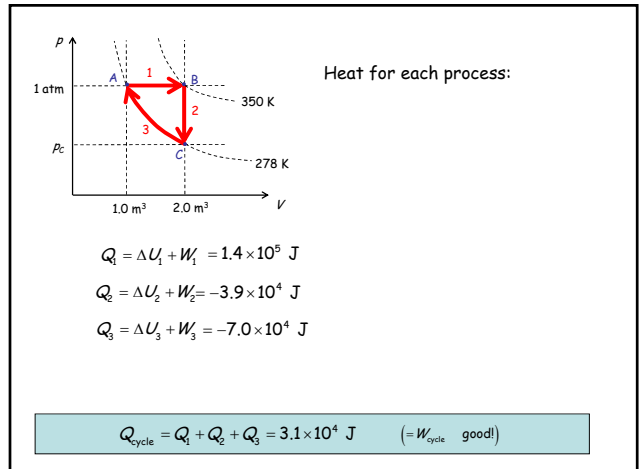
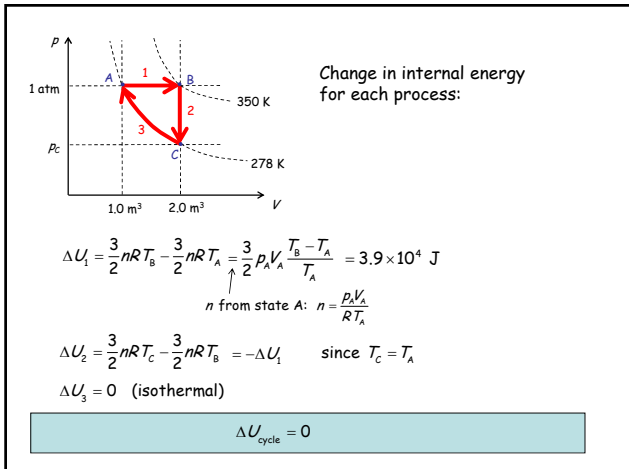
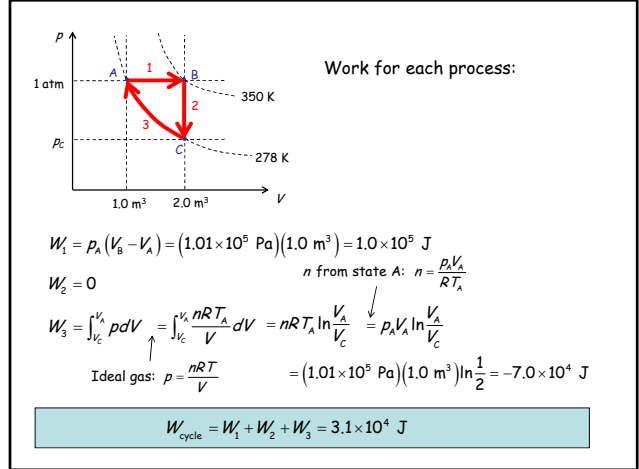
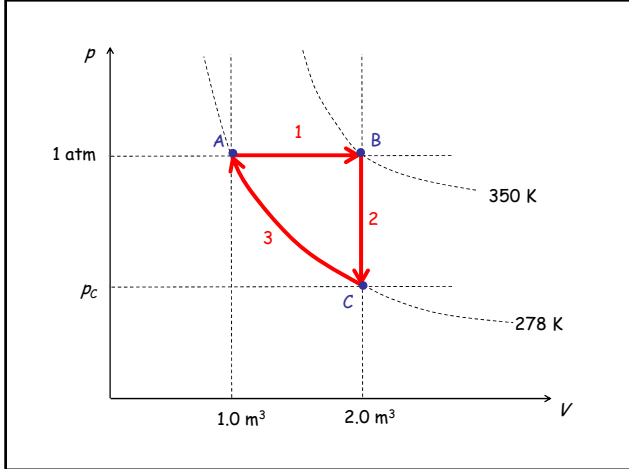
- An infinite number of **other processes** without any special name!



Example: Ideal gas cycle

An ideal monoatomic gas is trapped in a cylindrical container whose cap is a piston of negligible mass that can slide up and down the cylinder. The gas is initially at room temperature (298K) and occupies a volume of 1.0 m³. The piston is in its equilibrium position.

- (1) A mild heat source is then applied at the base of the container, and the gas is then slowly warmed up to 350K while the piston moves up to allow the gas to expand. Once the new temperature is reached, the volume of the gas is 2.0 m³. **Isobaric expansion**
- (2) The piston is locked in the new position and the gas is allowed to cool down to room temperature. **Isochoric cooling**
- (3) Finally, when room temperature is reached, the piston is pushed back manually but very slowly, so that the gas is allowed to remain in thermal equilibrium with the air in the room at all times. At the end, the piston is back in its initial position. **Isothermal compression**



Heat capacities

Take any process with a change in temperature, find heat Q . Their relation is the definition of heat capacity!

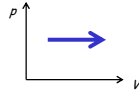
Process at **constant volume**:

$$dQ = nC_v dT$$



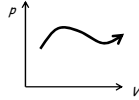
Process at **constant pressure**:

$$dQ = nC_p dT$$



Process X!

$$dQ = nC_x dT$$



Note: These are **molar** heat capacities.

Heat capacity at constant volume

Constant volume \Rightarrow no work $dU = dQ$

and we can write dQ in terms of dT : $dQ = nC_v dT$

$$\text{Thus, } C_v = \frac{1}{n} \frac{dU}{dT}$$

Monoatomic ideal gas $U = \frac{3}{2}nRT$ $C_v = \frac{3}{2}R$

Diatomic ideal gas $U = \frac{5}{2}nRT$ $C_v = \frac{5}{2}R$

Monoatomic solid $U = 3nRT$ $C_v = 3R$

Heat capacities (ideal gas)

Process at constant volume: $W = 0$

$$dU = dQ = nC_v dT$$

Process at constant pressure: $dW = pdV$

$$\begin{aligned} dU &= dQ - dW \\ &= nC_p dT - pdV \\ &= nC_p dT - nRdT \end{aligned}$$

$$\begin{aligned} pV &= nRT \\ pdV &= nRdT \end{aligned}$$

But: For the same change in temperature, the change in internal energy must be the same!

$$nC_v dT = nC_p dT - nRdT$$

$$C_p = C_v + R$$

Also, good news: we can use $dU = nC_v dT$ for any process!

Ratio of heat capacities

$$\gamma = \frac{C_p}{C_v}$$

Ideal gas:

Monoatomic

$$C_v = \frac{3}{2}R = 12.47 \frac{\text{J}}{\text{mol K}}$$

$$C_p = C_v + R = \frac{5}{2}R = 20.78 \frac{\text{J}}{\text{mol K}}$$

$$\gamma = \frac{C_p}{C_v} = \frac{\frac{5}{2}R}{\frac{3}{2}R} = \frac{5}{3} = 1.67$$

Diatomic

$$C_v = 5R/2 = 20.78 \frac{\text{J}}{\text{mol K}}$$

$$C_p = C_v + R = \frac{7}{2}R = 29.09 \frac{\text{J}}{\text{mol K}}$$

$$\gamma = \frac{C_p}{C_v} = \frac{\frac{7}{2}R}{\frac{5}{2}R} = \frac{7}{5} = 1.4$$

It works!

Table 19.1 Molar Heat Capacities of Gases at Low Pressure

Type of Gas	Gas	C_V (J/mol · K)	C_p (J/mol · K)	$C_p - C_V$ (J/mol · K)	$\gamma = C_p/C_V$
Monatomic	He	12.47	20.78	8.31	1.67
	Ar	12.47	20.78	8.31	1.67
Diatomic	H ₂	20.42	28.74	8.32	1.41
	N ₂	20.76	29.07	8.31	1.40
	O ₂	20.85	29.17	8.31	1.40
	CO	20.85	29.16	8.31	1.40
Polyatomic	CO ₂	28.46	36.94	8.48	1.30
	SO ₂	31.39	40.37	8.98	1.29
	H ₂ S	25.95	34.60	8.65	1.33

ACT: Different heating processes

Two containers have each 1 mole of monoatomic ideal gas inside. Heat is transferred into both, causing a 50°C rise in temperature. For container A, this happens at constant volume. For container B, this happens at constant pressure. Which of the following is correct?

- A. More heat is transferred into sample A
B. More heat is transferred into sample B
 C. Both samples absorb the same heat.

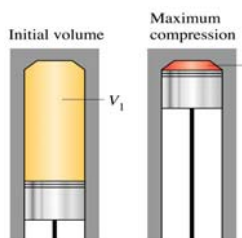
$$Q_A = nC_V\Delta T \quad C_p = C_V + R > C_V \quad Q_A < Q_B$$

$$Q_B = nC_p\Delta T$$

How much more?

$$Q_B - Q_A = n(C_p - C_V)\Delta T = nR\Delta T = (1 \text{ mole})\left(8.31 \frac{\text{J}}{\text{mol K}}\right)(50 \text{ K}) = 415 \text{ J}$$

Compression Stroke of Engines



If piston and cylinder are thermally insulated, no heat is transferred during compression, $Q = 0$ (adiabatic process)

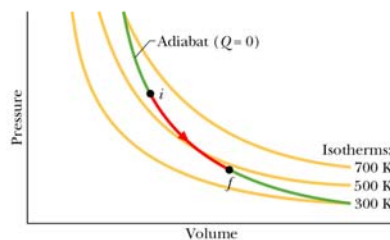
- In this stroke of an engine
- Gas is compressed → it does negative work
 - Internal energy increases
 - Temperature increases

Adiabatic Gas Expansion

Piston is insulated so that, as gas expands, $Q = 0$

$$\Delta U = Q - W = -W \quad \text{with } W > 0 \text{ (expansion), so } \Delta U < 0$$

↓
 $\Delta T < 0$
 Temperature decrease



Adiabatic curve for ideal gases: T and V

If $Q = 0$, $dU = -dW$

$$nC_V dT = -pdV$$

$$nC_V dT = -\frac{nRT}{V} dV$$

$$\frac{dT}{T} = -\frac{R}{C_V} \frac{dV}{V}$$

$$\frac{R}{C_V} = \frac{C_p - C_V}{C_V} = \gamma - 1$$

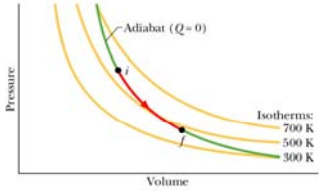
$$\frac{dT}{T} = -(\gamma - 1) \frac{dV}{V}$$

$$\ln T + (\gamma - 1) \ln V = \text{constant}$$

$$\boxed{TV^{\gamma-1} = \text{constant}}$$

$\gamma - 1 > 0$

For expansion, T decreases
For compression, T increases



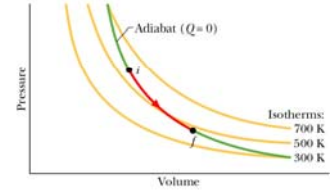
DEMO: Adiabatic compression

Adiabatic curve for ideal gases: p and V

$$TV^{\gamma-1} = \text{constant}$$

$$\frac{pV}{nR} V^{\gamma-1} = \text{constant}$$

$$\boxed{pV^\gamma = \text{constant}}$$



Work in adiabatic processes

If $Q = 0$, $W = -\Delta U$

$$\boxed{W = -nC_V \Delta T}$$

$$W = -nC_V \Delta T = -nC_V \frac{\Delta(pV)}{nR} = -\frac{\Delta(pV)}{\gamma - 1}$$

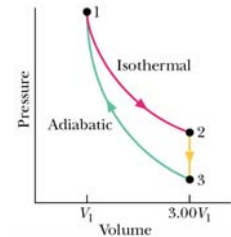
$$\boxed{W = -\frac{\Delta(pV)}{\gamma - 1}}$$

ACT: Cycle

An ideal gas expands isothermally to three times its initial volume. It then cools at constant volume, and is finally compressed adiabatically back to initial conditions.

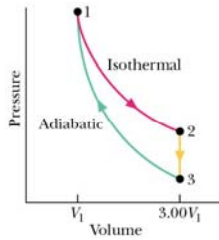
Sketch by yourself the cycle on a pV diagram

Compare with neighbors



Given p_1 , T_1 and V_1 .

- Calculate the temperature at which compression starts (3)
- Calculate heat removed during cooling (2) \rightarrow (3)



Adiabatic curve: $T_1 V_1^{\gamma-1} = T_3 V_3^{\gamma-1}$

$$T_3 = T_1 \left(\frac{V_1}{V_3} \right)^{\gamma-1} = T_1 \left(\frac{1}{3} \right)^{\gamma-1}$$

With $\gamma = \frac{5}{3}, \frac{7}{5}$... depending on type of gas.

Cooling at constant volume:

$$Q = nC_V (T_3 - T_2) = nC_V (T_3 - T_1)$$

With $C_V = \frac{3}{2}R, \frac{5}{2}R$... depending on type of gas.