FIRST LAW OF THERMODYNAMICS II

Intended Learning Outcomes – after this lecture you will learn:
1. adiabatic, isochoric, isobaric, and isotherm processes
2. free expansion and the corresponding temperature change
3. C_p and C_V of ideal gas
4. adiabatic process for ideal gas

Textbook Reference: Ch 19.5 – 19.8

Thermodynamic processes

Adiabatic process means $Q = 0$, it may be
1. a thermally insulated system where heat cannot enter or leave, e.g. in a thermal flask
2. a quick process where heat has no time to go in or out, e.g., by conduction

Adiabatic *expansion*, $W > 0 \Rightarrow \Delta U < 0$, usually leads to *cooling*

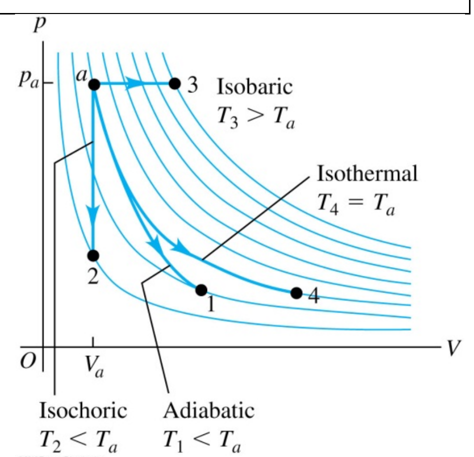
Adiabatic *compression*, $W < 0 \Rightarrow \Delta U > 0$, usually leads to *heating*

Demonstration: Adiabatic compression

Isochoric process means constant volume, e.g., in a close constant-volume container
Importance: *pdV* work is zero

Isobaric process means constant pressure, e.g., in atmospheric pressure
Importance: *pdV* work is $p(V_2 - V_1)$

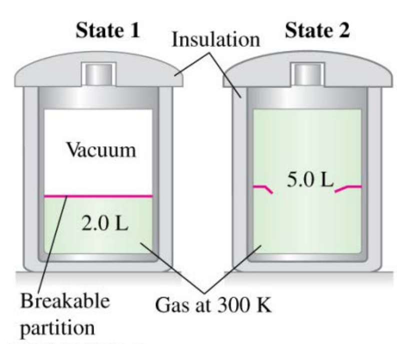
Isothermal process means constant temperature, i.e., *isotherms* in a pV diagram



Free Expansion

"free" means at no cost
An isolated system expands into vacuum:
- adiabatic, $Q = 0$;
- no work needed, $W = 0$;

then $\Delta U = 0$, internal energy does not change



Experimental results:

1. for dilute gas, no temperature change
2. for other gases, temperature drops

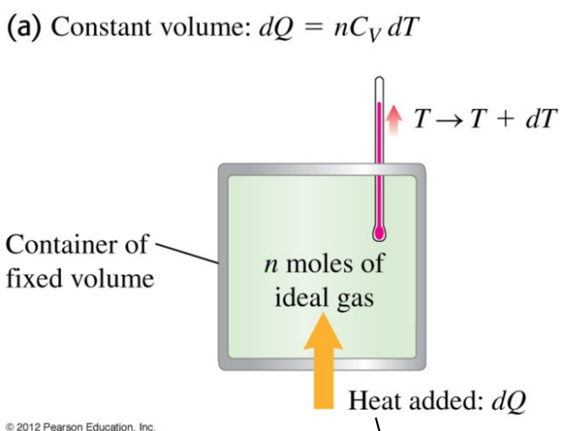
conclusion

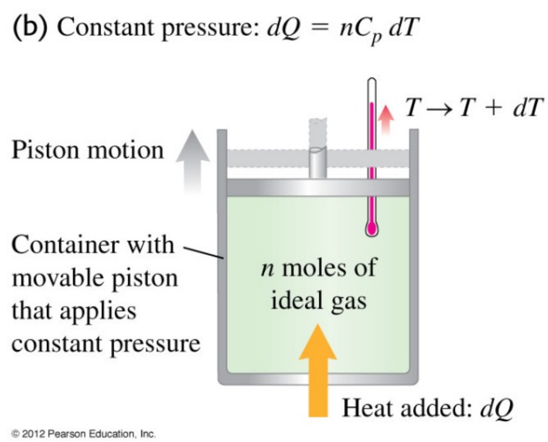
1. **for ideal gas, *T* depends on *U* (i.e., KE) only, not on *p* or *V*,** consistent with kinetic theory

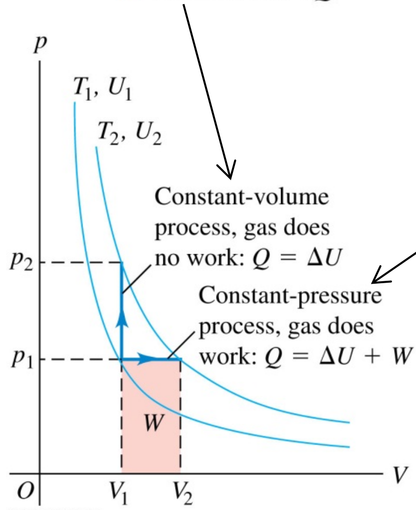
2. **for real gas** with intermolecular attraction, expansion → molecules farther apart → increase in PE (because molecules attract each other)
$\Delta U = 0$ → KE decreases
T drops → ***T* depends on KE** (*not U*)

Heat Capacities of an Ideal Gas

Raise the temperature of the same amount of ideal gas from T to $T+dT$ under two different conditions – constant volume and constant pressure, dU the same







$$\underbrace{dQ}_{nC_p dT} = \underbrace{dU}_{nC_V dT} + \underbrace{dW}_{pdV = nRdT}$$

$$\Rightarrow \quad \boxed{C_p = C_V + R}$$

Define the **ratio of heat capacities**

$$\gamma = \frac{C_p}{C_V} > 1$$

For monatomic ideal gas:

$f = 3, C_V = \frac{f}{2}R = \frac{3}{2}R \quad \Rightarrow \quad C_p = C_V + R = \frac{5}{2}R \quad \Rightarrow \quad \gamma = \frac{5}{3} = 1.67$

For diatomic ideal gas at room temperature (translation + rotation, no vibration because temperature not high enough to excite vibration):

$f = 5, C_V = \frac{f}{2}R = \frac{5}{2}R \quad \Rightarrow \quad C_p = C_V + R = \frac{7}{2}R \quad \Rightarrow \quad \gamma = \frac{7}{5} = 1.40$

⚠ For an ideal gas, $dU = n\frac{f}{2}RdT = nC_V dT$ always hold, irrespective of whether the volume remains constant in the process

Example 19.6 P. 656 Cooling your room

A room contains 2500 moles of air with $\gamma = 1.400$. The room is cooled from 35.0 ℃ to 26.0 ℃.

To find C_V of air:

$$\gamma = \frac{C_p}{C_V} = \frac{C_V + R}{C_V} = 1 + \frac{R}{C_V} \quad \Rightarrow \quad C_V = \frac{R}{\gamma - 1} = \frac{8.314\ \mathrm{J/mol\cdot K}}{0.400} = 20.79\ \mathrm{J/mol\cdot K}$$

The change in internal energy of air in this process is

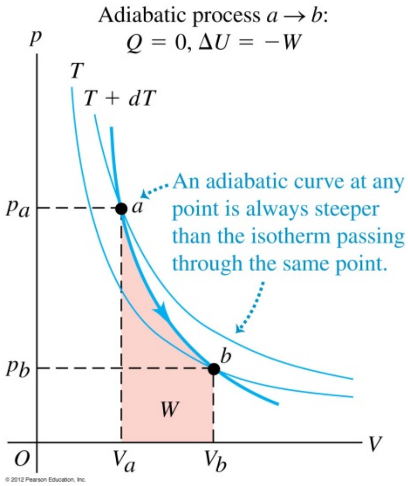
$$\Delta U = nC_V\Delta T = (2500\ \mathrm{mol})(20.79\ \mathrm{J/mol\cdot K})(-9\ \mathrm{K}) = -4.68 \times 10^5\ \mathrm{J}$$

Question

You have an ideal gas in a closed storage cylinder. It will be easiest to cool it from 30 ℃ to 20 ℃ if the gas is (monatomic / diatomic / polyatomic).

Answer: see inverted text on P. 656 of textbook

Adiabatic Process for Ideal Gas



Qualitatively:
for an ideal gas, U depends on T only
adiabatic expansion: $W > 0, \Delta U < 0 \;\Rightarrow$ cooling
adiabatic compression: $W < 0, \Delta U > 0 \;\Rightarrow$ heating

Analytically:

$$dU = \frac{f}{2} nRdT$$

for an adiabatic process

$$dU = -dW = -pdV = -\frac{nRT}{V} dV$$

$$\Rightarrow \qquad \frac{dT}{T} + \frac{2}{f}\frac{dV}{V} = 0$$

$$\gamma - 1 = \frac{C_p - C_V}{C_V} = \frac{R}{\frac{f}{2}R} = \frac{2}{f}$$

$$\frac{dT}{T} + (\gamma - 1)\frac{dV}{V} = 0$$

⚠ dT and dV are of opposite signs, i.e., if $dV > 0$ (expansion), $dT < 0$ (cooling), etc.
Integrating, get

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

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

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

Eliminate T by using $T = pV/nR$

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

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

Work done by the ideal gas in an adiabatic process

$$W = -\Delta U = n\frac{f}{2}R(T_1 - T_2)$$

$$= n\frac{f}{2}R\left(\frac{p_1V_1}{nR} - \frac{p_2V_2}{nR}\right)$$

$$= \frac{p_1V_1 - p_2V_2}{2/f}$$

$$\boxed{W = \frac{1}{\gamma - 1}(p_1V_1 - p_2V_2)}$$

⚠ note that on the RHS the term is $(p_1V_1 - p_2V_2)$, *not* $(p_2V_2 - p_1V_1)$

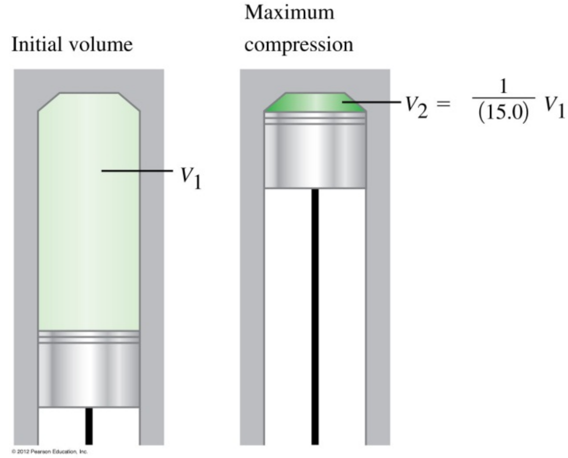
Example 19.7 P. 659 Adiabatic compression in a diesel engine

A cylinder of a diesel engine contains air with $\gamma = 1.400$, initially at 1.01×10^5Pa, 27 °C and initial volume 1.00 L. The air is compressed to $1/15.0$ of its initial volume.

The final temperature and pressure are

$$T_2 = T_1 \left(\frac{V_1}{V_2}\right)^{\gamma-1} = (300\text{ K})(15.0)^{0.4} = 886\text{ K}$$

$$p_2 = p_1 \left(\frac{V_1}{V_2}\right)^{\gamma} = (1.01 \times 10^5\text{Pa})(15.0)^{1.4}$$
$$= 44.8 \times 10^5\text{Pa}$$



Work done *by* the gas during the compression

$$W = \frac{1}{1.400 - 1}\left[(1.01 \times 10^5\text{Pa})(1.00 \times 10^{-3}\text{m}^3) - (44.8 \times 10^5\text{Pa})\left(\frac{1.00 \times 10^{-3}\text{m}^3}{15.0}\right)\right]$$
$$= -494\text{ J}$$

⚠ note the sign of *W*

Question

If you compress an ideal gas to half of its initial volume, arrange the final pressure in the following cases in descending order:

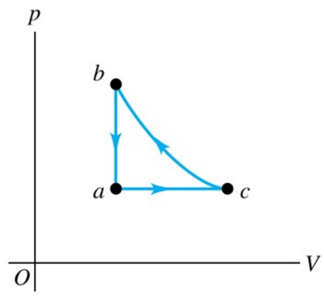
a) a monatomic gas compressed adiabatically
b) a monatomic gas compressed isothermally
c) a diatomic gas compressed adiabatically
d) a diatomic gas compressed isothermally

Answer: see inverted text on P. 659 of textbook

Clicker Questions

Q19.12

An ideal gas is taken around the cycle shown in this p-V diagram, from a to c to b and back to a. Process $c \rightarrow b$ is adiabatic. For process $c \rightarrow b$,



A. $Q > 0$, $W > 0$, $\Delta U = 0$

B. $Q > 0$, $W > 0$, $\Delta U > 0$

C. $Q = 0$, $W > 0$, $\Delta U < 0$

D. $Q = 0$, $W < 0$, $\Delta U > 0$

E. $Q < 0$, $W < 0$, $\Delta U = 0$

Q19.13

When an ideal gas is allowed to expand *isothermally* from volume V_1 to a larger volume V_2, the gas does an amount of work equal to W_{12}. If the same ideal gas is allowed to expand *adiabatically* from volume V_1 to a larger volume V_2, the gas does an amount of work that is

A. less than W_{12}.

B. greater than W_{12}.

C. equal to W_{12}.

D. either A or B, depending on the ratio of V_2 to V_1.

E. any of A, B, or C, depending on the ratio of V_2 to V_1.

Ans: Q19.12) D, Q19.13) A