

→ Experiments show that  $\Delta U$  is path independent – the way in which this occurs does NOT matter.

$$dU = dQ - dW$$

## Lecture 6: The First Law of Thermodynamics

- In a cyclic thermodynamic process:

$$Q = W \rightarrow \Delta U = 0$$

You eat a hot fudge sundae with an energy content of 900 kilo-calories (1 kilo-calorie = 4190 J). How high would you have to climb up several flights of stairs to work off this energy? Assume a weight of 60.0 kg.

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

$$Q = 900 \text{ kcal} \times 4190 \text{ J/kcal} = 3.77 \times 10^6 \text{ J}$$

$$Q = W = mgh \Rightarrow h = \frac{Q}{mg} = \frac{3.77 \times 10^6 \text{ J}}{(60.0 \text{ kg})(9.80 \text{ m s}^{-2})} = 6410 \text{ m}$$

n.b. this assumes all the energy consumed is converted with 100% efficiency into mechanical work.

1 g water ( $V = 1 \text{ cm}^3$ ) becomes  $1671 \text{ cm}^3$  of steam when boiled at  $p = 1 \text{ atm}$ . What is  $\Delta U$ ?

$$\Delta U = Q - W$$

$$Q = mL_v = (10^{-3} \text{ kg})(2.256 \times 10^6 \text{ J kg}^{-1}) = 2256 \text{ J}$$

$$W = p(V_2 - V_1) = (1.013 \times 10^5 \text{ Pa})(1671 - 1) \text{ cm}^3 = 169 \text{ J}$$

$$\Delta U = 2256 \text{ J} - 169 \text{ J} = 2087 \text{ J}$$

Note: only a small amount of energy is lost to doing work via expansion. Increase in  $U$  goes into increasing the potential energy associated with intermolecular forces (not kinetic energy as it is *isothermal*).

- When pressure is lower, boiling point decreases.
- There are several types of thermodynamic processes.
  - Adiabatic:  $Q=0$  – no heat is added/removed (isolated).
  - Isochoric:  $\Delta V=0$  – constant volume.
  - Isobaric:  $\Delta P=0$  – constant pressure.
  - Isothermal:  $\Delta T=0$  – constant temperature.

### 1. adiabatic:

$$Q = 0 \Rightarrow \Delta U = -W$$

### 2. isochoric:

$$dV = 0 \Rightarrow W = 0 \Rightarrow \Delta U = Q$$

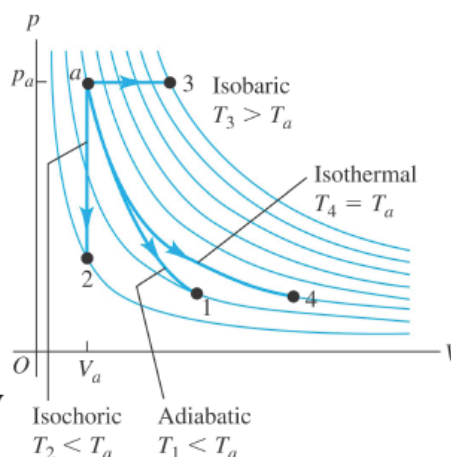
### 3. isobaric:

$$p = \text{const.} \Rightarrow W = p(V_2 - V_1)$$

### 4. isothermal:

$$\Delta T = 0 \Rightarrow \Delta U = 0 \Rightarrow Q = W$$

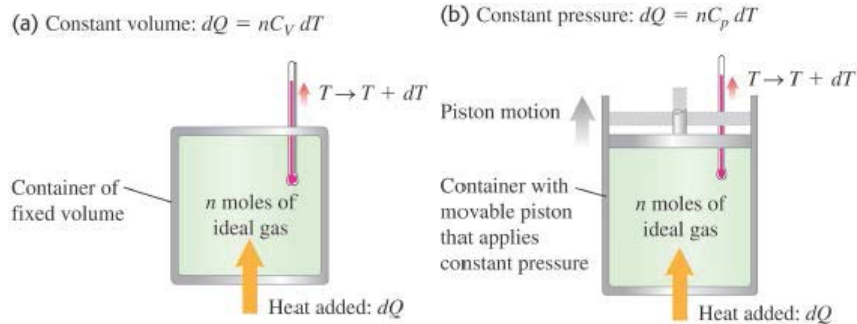
(for ideal gases only)



- For an ideal gas, internal energy depends only on  $T$  – not  $p$  or  $V$ .
  - Remember that  $T$  is a measure of how much energy there is per molecule – in an ideal gas, changing volume or pressure with constant temperature means no change in energy per molecule and hence, no change in internal energy.
- In free expansion,  $Q=0$  and  $W=0$  and hence,  $\Delta U=0$ .
  - $P$  and  $V$  change but  $T$  is constant.

## Lecture 7: Heat Capacity of an Ideal Gas

- Raising the temperature of an ideal gas requires different amounts of heat for constant volume and pressure.



→ For (a):

$$dU = dQ_V$$

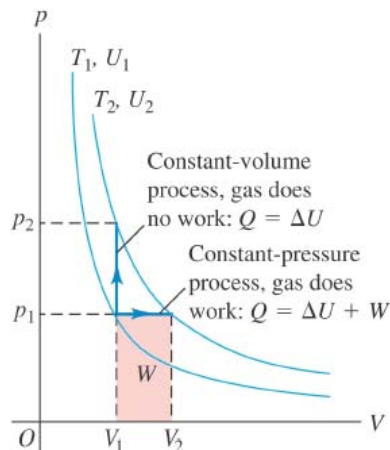
→ For (b):

$$dU = dQ_P - dW$$

- Note:**  $U$  only depends on temperature for ideal gases.

- For a given  $dT$ , an isobaric process requires more heat than an isochoric process because in an isobaric process, work is done.

→  $\Delta U$  is path dependent (remember, area under the curve).



$$nC_V dT = nC_P dT - pdV = nC_P dT - nRdT$$

$$\rightarrow C_P = C_V + R$$

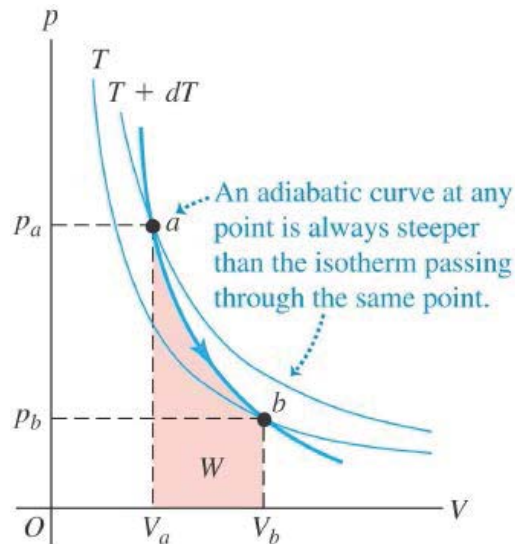
- Adiabatic index (or heat capacity ratio) is a ratio of specific heats.

$$\gamma = \frac{C_P}{C_V} = 1 + \frac{R}{C_V}$$

→  $C_V$  is higher for polyatomic gases as there are more degrees of freedom: rotational and vibrational.

- In an adiabatic process,  $Q=0$  then  $\Delta U = -W$

$$nC_V dT = -pdV = \frac{-nRTdV}{V}$$



1. fire piston

**adiabatic heating**

$$\Rightarrow \Delta T > 0$$

$\Rightarrow$  combustion of cotton wool



2. fire extinguisher

**adiabatic cooling**

$$\Rightarrow \Delta T < 0$$

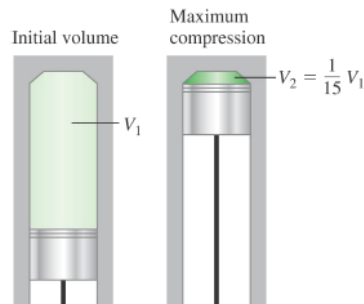
$\Rightarrow$  sublimation of  $\text{CO}_2$



**Ex. 19.7** Adiabatic compression in a diesel engine.

Rapid compression of air to  $\frac{1}{15}$  of initial volume, mostly  $\text{O}_2$  and  $\text{N}_2$ , so

$$\gamma = \frac{7}{5} = 1.40$$



$$T_1 = 27^\circ\text{C} = 300\text{ K}$$

$$p_1 = 1\text{ atm} = 1.01 \times 10^5\text{ Pa}$$

$$T_2 = T_1 \left( \frac{V_1}{V_2} \right)^{\gamma-1} = 886\text{ K} = 613^\circ\text{C}$$

$$p_2 = p_1 \left( \frac{V_1}{V_2} \right)^{\gamma} = 44.8 \times 10^5\text{ Pa} = 44\text{ atm}$$

Diesel fuel is injected and promptly ignites at  $(T_2, p_2)$ .

Calculate the work done on the gas in the previous example if the initial volume is  $V_1 = 1.00\text{ L} = 1.00 \times 10^{-3}\text{ m}^3$ . Use  $C_V = 20.8\text{ J mol}^{-1}\text{ K}^{-1}$

$$W = nC_V(T_1 - T_2)$$

$$T_1 - T_2 = 300\text{ K} - 886\text{ K} = -586\text{ K}$$

Use ideal gas law to calculate  $n$ :

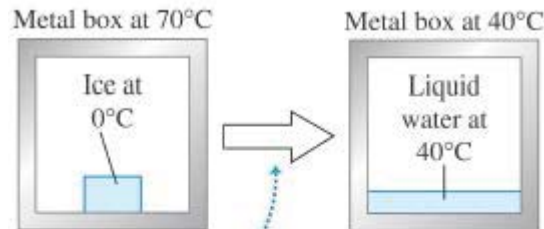
$$n = \frac{pV}{RT} = \frac{p_1 V_1}{RT_1} = \frac{(1.01 \times 10^5\text{ Pa})(1.00 \times 10^{-3}\text{ m}^3)}{(8.314\text{ J mol}^{-1}\text{ K}^{-1})(300\text{ K})} = 0.0405\text{ mol}$$

$$\Rightarrow W = (0.0405\text{ mol})(20.8\text{ J mol}^{-1}\text{ K}^{-1})(-586\text{ K}) = -494\text{ J}$$

## Lecture 8: Directions of Thermodynamic Processes

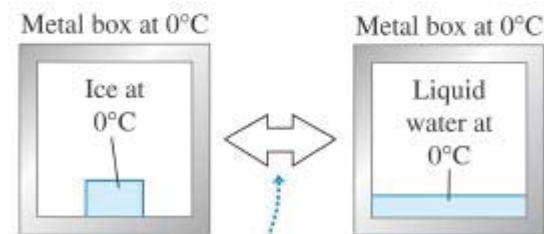
- Irreversible processes are those that are spontaneous in only one direction – this includes most natural processes.
- Reversible processes are those that reach equilibrium and can occur in both directions.

(a) A block of ice melts *irreversibly* when we place it in a hot (70°C) metal box.



Heat flows from the box into the ice and water, never the reverse.

(b) A block of ice at 0°C can be melted *reversibly* if we put it in a 0°C metal box.



By infinitesimally raising or lowering the temperature of the box, we can make heat flow into the ice to melt it or make heat flow out of the water to refreeze it.

- A heat engine is any device that converts heat into work.

$$Q = Q_H + Q_C = Q_H - |Q_C|$$

$$e = \frac{W}{Q_H} = 1 - \left| \frac{Q_C}{Q_H} \right|$$

→ Example: steam engines, combustion engines, Stirling engines etc.

