11 – Thermodynamics

Heat and heat capacity, Second Law of thermodynamics

1) $T_A > T_B$ 2) $T_A = T_B = T$
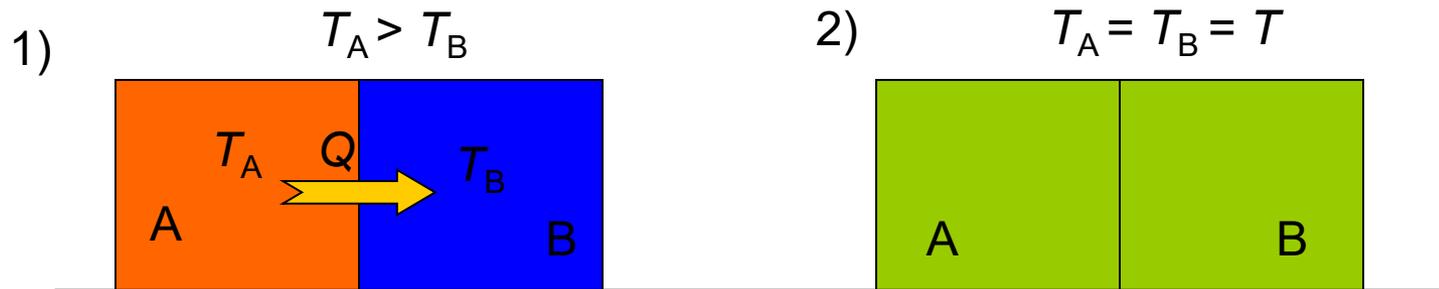
Heat Q is transferred from the hotter body to the colder one until temperatures equilibrate – this is the Second Law of thermodynamics.

Historically heat was thought to be a kind of a liquid (caloric) but it is in fact just the energy transferred between the bodies without doing work.

One calory (1 cal) is defined as the amount of heat needed to raise the temperature of 1 g of water by 1°C (or 1 K). For small temperature changes ΔT there is a linear relation

$$Q = C\Delta T = mc\Delta T$$

C – heat capacity in cal/K
m – the mass of the system in g
c – specific heat capacity in cal/(g K)

By definition, c = 1 cal/(g K) for water. Bringing water into thermal contact with other materials and thus letting the heat flow from one to another and measuring temperature changes of both allows to define heat capacities of other substances. Most of them have c smaller than water. The experimental device is the calorimeter – a thermally isolated pot with a thermometer.

1

Calorimeter

Problem: In one experiment, a student throws 100 g lead [c_L=0.0305 cal/(g K)] at 0°C into 1 liter water at 100°C. In another experiment she adds 100 g water at 0°C to 1 liter water at 100°C. Compare the resulting temperatures in both cases.

Solution: Consider a general case of adding substances with heat capacities c_A and c_B, masses m_A and m_B, and temperatures T_A and T_B, The resulting temperature is T. The heat flows from A to B, thus the sum of heat recieved by A and by B is zero:

$$0 = Q_A + Q_B = m_A c_A \Delta T_A + m_B c_B \Delta T_B = m_A c_A (T - T_A) + m_B c_B (T - T_B)$$

Solving this equation for *T* one obtains

$$T = \frac{m_A c_A T_A + m_B c_B T_B}{m_A c_A + m_B c_B}$$

Now for the first experiment

$$T_1 = \frac{1000 \times 1 \times 100 + 100 \times 0.0305 \times 0}{1000 \times 1 + 100 \times 0.0305} = 100 \frac{1}{1 + 100 \times 0.0305/1000} = 100 \frac{1}{1 + 0.00305} \cong 100(1 - 0.00305) = 99.695°C$$

(a very small cooling effect)

For the second experiment

$$T_2 = \frac{1000 \times 1 \times 100 + 100 \times 1 \times 0}{1000 \times 1 + 100 \times 1} = 100 \frac{1}{1 + 100 \times 1/1000} = 100 \frac{1}{1 + 0.1} = 90.91°C \quad \text{(Cooling by about 9°C)}$$

In this experiment, one can measure c_B, if c_A is known:

$$c_B = -\frac{m_A(T - T_A)}{m_B(T - T_B)} c_A$$

2

Latent heat of phase transformations

Heat flow to or from an object can cause not only its warming or cooling but also its phase transformations such as freezing or melting that occur without change of temperature. Heat required to cause phase transitions is called <u>latent heat</u>, Q_L, and the <u>specific latent heat</u> is $q_L = Q_L / m$, so that $Q_L = m \, q_L$.

Coexistence of different phases (such as water and ice) makes the temperature stable, since heat flowing into or out of the system causes phase transition but not heating or cooling.

Example: The latent heat of ice melting is 80 cal/g and the latent heat of water evaporation is 539 cal/g. To melt 1 g of ice at 0°C, warm it up to 100°C and evaporate the water, one has to supply the following amounts of heat:

- 80 cal to melt the ice
- 100 cal to warm the water from 0°C to 100°C
- 539 cal to evaporate the water

Conversely, the latent heat of the water freezing is -80 cal/g and the latent heat of the water vapor condensing is -539 cal/g.

While the heat required for melting is comparable with the heat required for heating (that is already impressive!) the heat required for evaporation is much higher. The latent heat of evaporation is so high because this heat must be sufficient to overcome the attractive interaction between the molecules and bring them at large distances from each other. Inversely, condensation of water vapour releases a huge amout of latent heat that is extremely damageable in the case of vapor burns.

3

Problem. In one experiment, a barman throws 100 g ice at 0°C into 1 liter water at 10°C. Find resulting temperature.

Solution. Assuming that the system ice (A)+water (B) is thermally isolated and all ice melts, one can write down the condition of the zero heat received by the system as

$$0 = Q_A + Q_B = m_A q_L + m_A c_A (T - T_A) + m_B c_B (T - T_B)$$

In this equation it is taken into account that the latent heat is received by the ice for melting and then the further heat is received by the resulting water to warm it up from $T_A = 0°C$ to the final temperature T. Solving this equation for T, one obtains

$$T = \frac{-m_A q_L + m_A c_A T_A + m_B c_B T_B}{m_A c_A + m_B c_B} = \frac{-m_A q_L + m_B c_B T_B}{m_A c_A + m_B c_B}.$$

In the second expression, we have taken into account $T_A = 0°C$. The solution above is valid if $T > 0$, that is, $m_A q_L < m_B c_B T_B$. This means that there is not too much ice and all ice melts. If this is not satisfied, ice melts only partially and in the final state there is a mixture of ice and water at $T = 0°C$. In our case,

$$T = \frac{-100 \times 80 + 1000 \times 1 \times 10}{100 \times 1 + 1000 \times 1} = \frac{2000}{1100} = 1.82°C > 0°C,$$

so that the solution is valid. Another case is considered in the next slide.

Problem. In one experiment, a barperson throws 150 g ice at 0°C into 1 liter water at 10°C. Find resulting state of the system.

Solution. We assuming that the system ice (A)+water (B) is thermally isolated. As there is a lot of ice, one can suspect that not all ice melts, and the final state is a mixture of water at $T = 0$ and the rest of the ice with mass m_{Af}. The condition of the zero heat received by the system reads

$$0 = Q_A + Q_B = (m_A - m_{Af})q_L + m_B c_B (T - T_B), \qquad T = 0$$

Solving this equation for m_{Af}, one obtains

$$m_{Af} = m_A - \frac{m_B c_B T_B}{q_L}.$$

The solution above is valid if $m_{Af} > 0$, that is, $m_A q_L > m_B c_B T_B$. This condition is opposite to that in the preceding slide. This means that there is a lot of ice and not all ice melts. If this condition is not satisfied, ice melts completely and in the final temperature $T > 0°C$. In our case,

$$m_{Af} = 150 - \frac{1000 \times 1 \times 10}{80} = 150 - 125 = 25 \; g,$$

so that the solution is valid. Another case is considered in the preceding slide.

Rubbing a surface of a solid object or stirring a liquid shows that making work on the object can cause increase of its temperature, that is, the effect of making work may be similar to that of a heat supply. It shows that heat is just another form of work: Both making work on an object and supplying heat to it leads to the increase of its internal energy U

J. P. Joule (1818-1889) showed this equivalence and found mechanical equivalent of the calory in his historical falling mass experiment
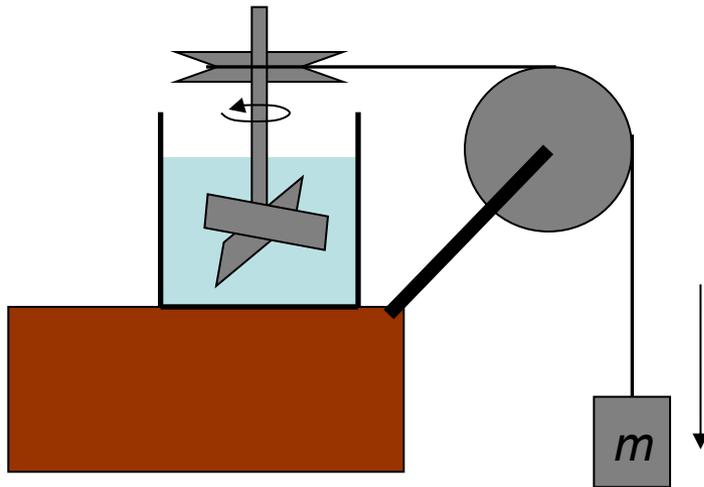
Joule found that 4.19 J of work is required to raise the temperature of 1 g of water by 1°C. The same effect may be achieved by supplying 1 cal of heat. This means

$$1 \text{ cal} = 4.19 \text{ J}$$

(Generalized energy conservation law)

$$\Delta U = Q + W$$

Here ΔU is the change of the internal energy of the system
   (potential energy due to interaction of molecules plus their kinetic energy)
Q is the heat received by the system
W is the work done on the system (compression or expansion). <u>Dissipative</u> work (rubbing, stirring, etc.) is counted as heat.

In infinitesimal form (all terms are very small)

$$\Delta U = \Delta Q + \Delta W = \Delta Q - P\Delta V$$

$-P\Delta V$ is so-called <u>configurational</u> work on the body derived below.

(See the sketch. If the body expands, $\Delta l > 0$, the work on the body is negative. The external force is directed to the left to contain the gas. Use the formulas for pressure and volume.)

Work done on the system (by the external force):

$$\Delta W = -F\Delta l = -PS\Delta l = -P\Delta V$$

Work done *by* the system (itself):

$$\Delta W_{by\ the\ system} = -\Delta W = P\Delta V$$
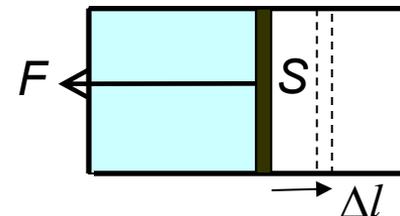
S – cross-sectional area

7

Energy and heat capacity of the ideal gas

For ideal gases (rarified gases) the potential energy is negligibly small, and thus *U* is kinetic energy that is proportional to the temperature. From the kinetic theory of *monoatomic* gases (preceding lecture) follows

$$U = N\langle\varepsilon\rangle = N\frac{3}{2}k_B T$$

This is the kinetic energy corresponding to the linear motion along three different directions in space.

Now consider processes with constant volume, $\Delta V = 0$, and with no dissipative work (rubbing, stirring). In this case, the first law of thermodynamics has the form

$$\Delta U = \Delta Q$$

Using the definition of the heat capacity and the formula for U above, one obtains

$$\Delta Q = C\Delta T = \Delta U = N\frac{3}{2}k_B \Delta T$$

so that

$$C = N\frac{3}{2}k_B$$

Diatomic gases (molecules consisting of two atoms) and multiatomic gases additionally have rotational kinetic energy, so that their internal energy and heat capacity are higher.

If a gas is thermally isolated so that $Q = 0$ (<u>adiabatic process</u>) and a negative work $W < 0$ is done on the gas (the gas expands), its internal energy U decreases, and its temperature T decreases, too. On the contrary, adiabatic compression of a gas leads to the increase of its temperature. For this reason, the adiabatic process is described by a steeper curve in the P-V diagram than the isothermic process.

Adiabatic process, $Q = 0$
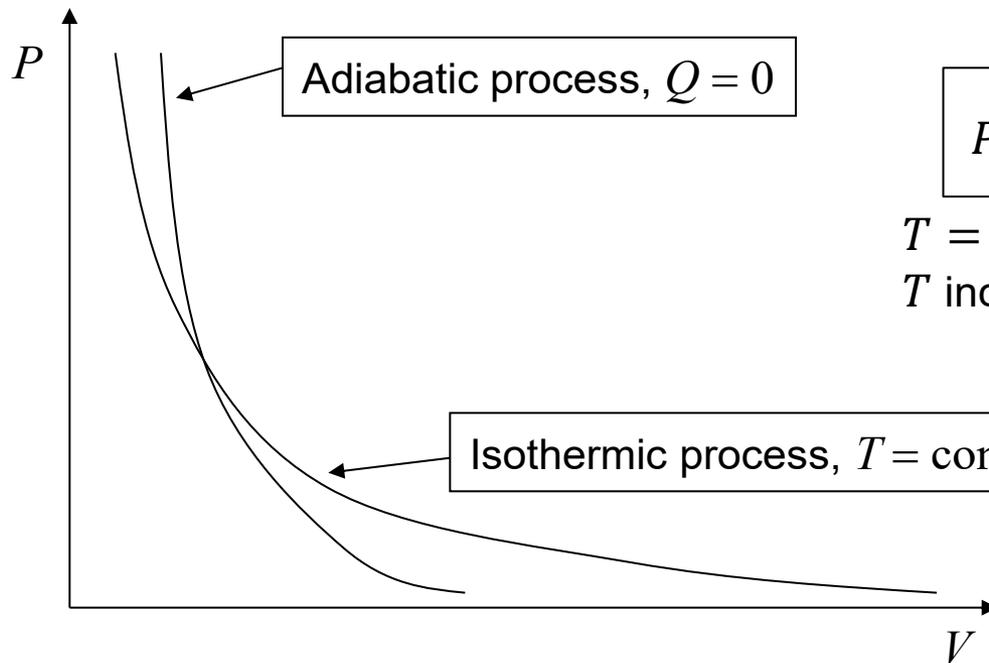
$$P = \frac{N k_B T}{V}$$

$T = const$ in the isothermic process
T increases with compression
in the adiabatic process

Isothermic process, $T = \text{const}$

On the contrary, isothermic process on an ideal gas conserves its internal energy, thus $Q + W = \Delta U = 0$ and the positive work done on compressing the gas is all given away as heat, $Q < 0$.

Problem: Work of 1500 J is done on an ideal gas, but the internal energy increases by only 800 J. What is the amount and the direction of heat flow, into or out of the system?

Solution: use

$$\Delta U_{\text{of the object}} = Q_{\text{Added to the object}} + W_{\text{Done on the object}}$$

with *W* = 1500 J and *ΔU* = 800 J. We find

$$Q = \Delta U - W = 800 - 1500 = -700 \text{ J}$$

Q < 0 thus the heat flows out of the system

Problem: An ideal gas is slowly compressed at a constant pressure of 2.0 atm from 10 L to 2 L. Then the temperature and pressure rised at constant volume until the temperature reached the initial value. Calculate: (a) the total work done on the gas; (b) the total amount of heat recieved by the gas.

Note that here we consider the work done by the gas, not the work done on the gas, so that the sign in front of the work is different!

Given: V_A = 10 L, V_B = 2 L, P_A = P_B = 2 atm, T_A = T_C.

To find: *W*-?, *Q*-?

Solution: Work is done on the path AB only
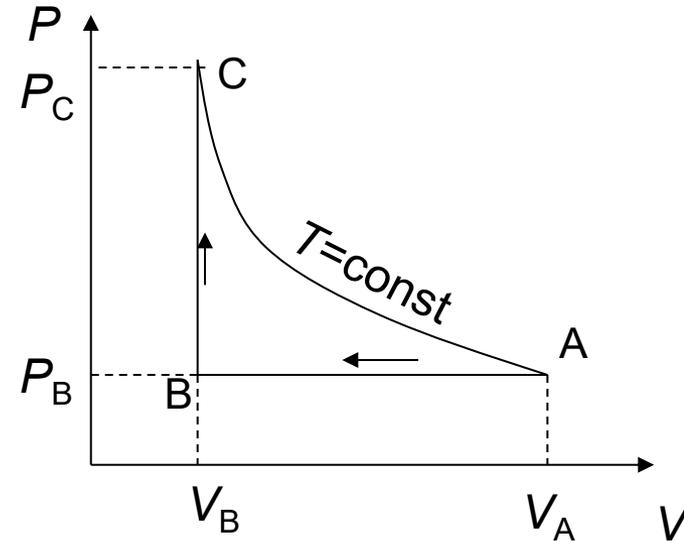
$$W = -P\Delta V = -P_A(V_B - V_A) = -2 \times 1.013 \times 10^5 (2 - 10) \times 10^{-3} = 1.62 \times 10^3 \, J$$

To calculate the total received heat Q, we note that the temperature in the final state is the same as that in the initial state. Since for ideal gases the internal energy depends on temperature only, we conclude that the internal energy in the whole process does not change, U_A = U_C, or ΔU = 0. From the first law of thermodynamics one then obtains

$$0 = \Delta U = Q + W \quad \Rightarrow \quad Q = -W = -1.62 \times 10^3 \, J$$

11