Heat capacity of gases

Related topics

Equation of state for ideal gases, 1st law of thermodynamics, universal gas constant, degree of freedom, mole volumes, isobars, isotherms, isochors and adiabatic changes of state.

Principle and task

Heat is added to a gas in a glass vessel by an electric heater which is switched on briefly. The temperature increase results in a pressure increase, which is measured with a manometer. Under isobaric conditions a temperature increase results in a volume dilatation, which can be read from a gas syringe. The molar heat capacities C_V and C_p are calculated from the pressure or volume change.

Equipment

Precision manometer	03091.00	1
Barometer/Manometer, hand-held	07136.00	1
Digital counter, 4 decades	13600.93	1
Digital multimeter	07134.00	2
Aspirator bottle, clear gl. 1000 ml	34175.00	1
Gas syringe, 100 ml	02614.00	2
Stopcock, 1-way, straight, glass	36705.00	1
Stopcock, 3-way, t-sh., capil., glass	36732.00	1
Rubber stopper, d 22/17 mm, 3 holes	39255.14	1
Rubber stopper, d 32/26 mm, 1 hole	39258.01	1
Rubber tubing, d 7 mm	39282.00	2
Nickel electrode, d 3 mm, w. socket	45231.00	2
Nickel electrode 76×40 mm	45218.00	1
Chrome-nickel wire, d 0.1 mm, 100 m	06109.00	1
Scissors, straight, l 140 mm	64625.00	1
Push-button switch	06039.00	1
Connection box	06030.23	1
PEK carbon resistor 1 W 5 % 1 kOhm	39104.19	1
PEK electrol.capacitor 2 mmF/ 250 V	39105.29	1
Connecting cord, 500 mm, yellow	07361.02	3
Connecting cord, 500 mm, red	07361.01	1
Connecting cord, 750 mm, red	07362.01	1
Connecting cord, 500 mm, blue	07361.04	4
Tripod base -PASS-	02002.55	1
Retort stand, h 750 mm	37694.00	2
Universal clamp	37715.00	2
Right angle clamp	37697.00	2

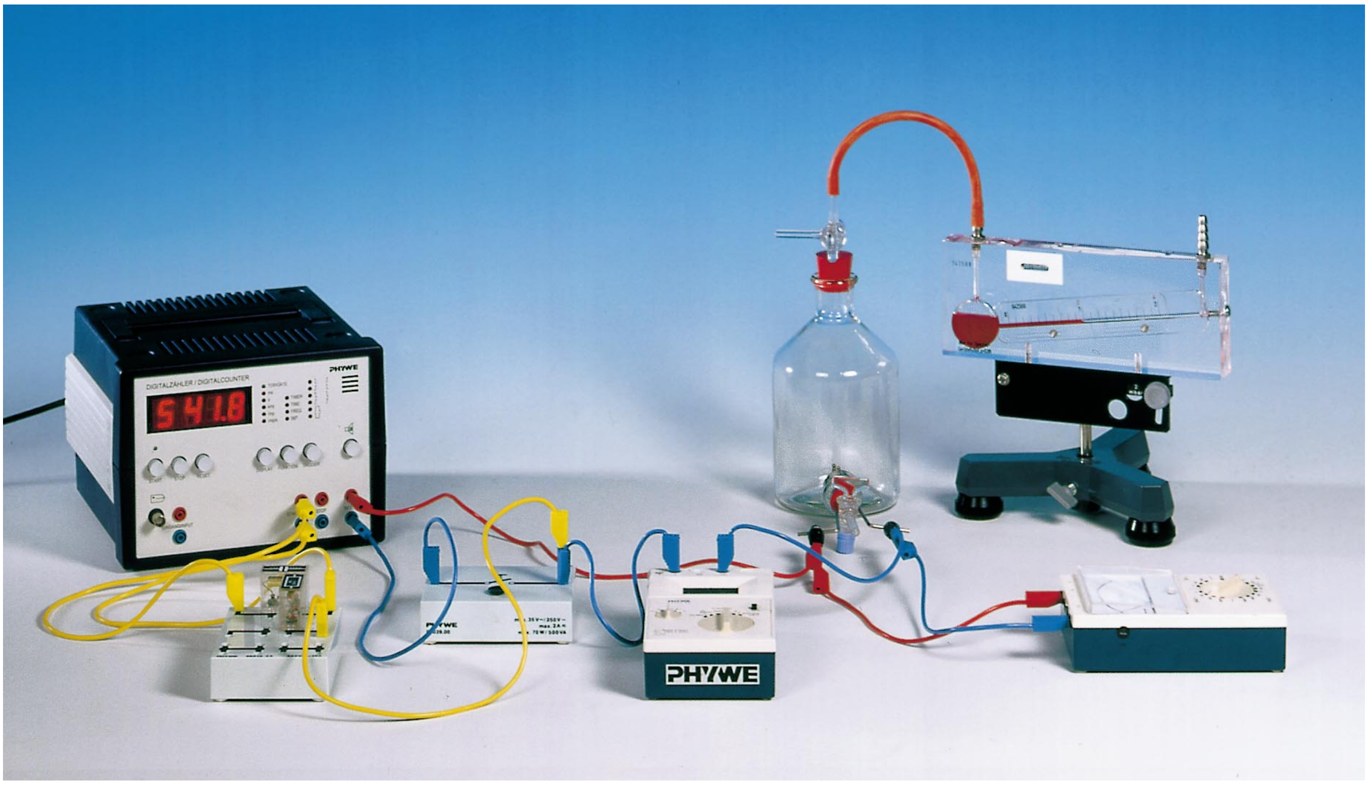
Problems

Determine the molar heat capacities of air at constant volume C_V and at constant pressure C_p.

Set-up and procedure

Perform the experimental set-up according to Figs. 1 and 2. Insert the two nickel electrodes into two holes in the three-hole rubber stopper and fix the terminal screws to the lower ends of the electrodes. Screw two pieces of chrome nickel wire, which are each about 15 cm long, into the clamps between these two electrodes so that they are electrically connected in parallel. The wires must not touch each other. Insert the one-way stopcock into the third hole of the stopper and insert the thus-prepared stopper in the lower opening of the bottle.

Fig. 1: Experimental set-up (C_V).



The 5 V output of the electrical 4-decade digital counter serves as the power source. The electrical circuit is illustrated in Fig. 3.

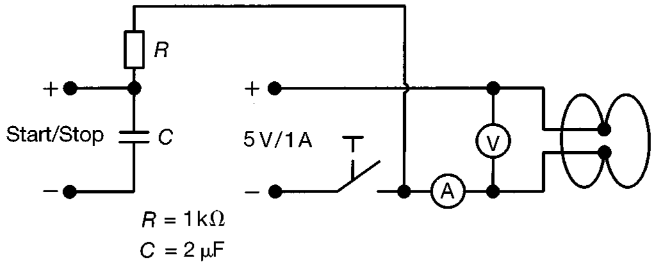
To determine C_V, connect the precision manometer to the bottle with a piece of tubing. To do this, insert the second stopper, which has been equipped with the three-way stopcock, into the upper opening of the bottle (Fig. 1). The manometer must be positioned exactly horizontally. Read the pressure increase immediately after cessation of the heating process.

The manometer must be filled with the oil which is supplied with the device. The scale is now calibrated in hPa. The riser tube of the manometer must be well wetted before each measurement.

Start the measuring procedure by activating the push-button switch. The measuring period should be as short as possible (less than one second). Determine the current which flows during the measurement and the voltage separately at the end of the measuring series. To achieve this, connect one of the digital multimeters in series as an ammeter and the other in parallel as a voltmeter.

Perform at least 10 measurements. After each measurement, perform a pressure equalisation with the ambient atmospheric pressure by opening the three-way cock. The electrical current which flows during the measurements must not be too strong, i.e. it must be sufficiently weak to limit the pressure increase due to the heating of the gas to a maximum of 1 hPa.

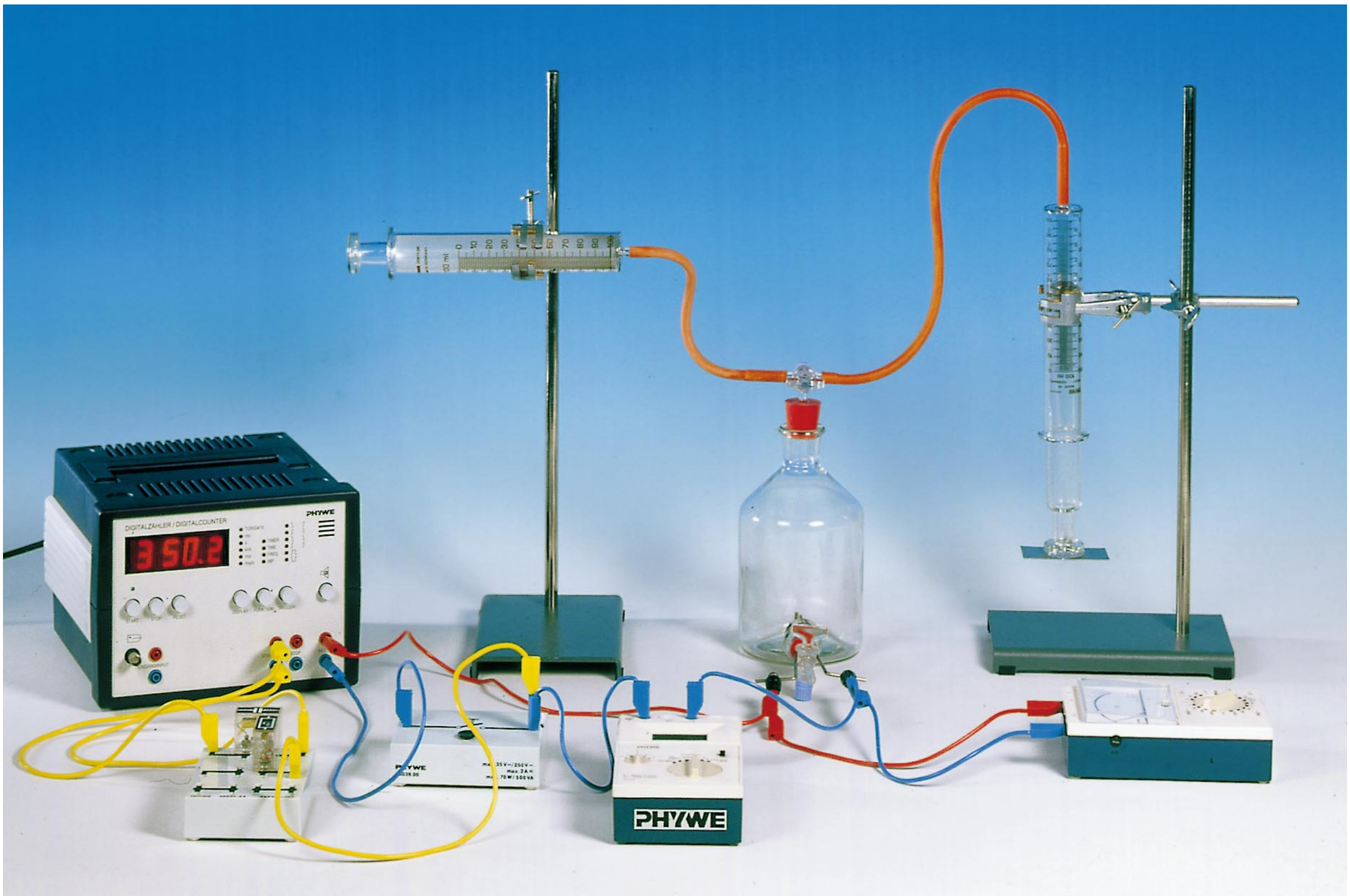
Fig. 3: Connecting the counter-timer.



For this reason it may be necessary to use only one heating wire.

In order to be able to determine C_p replace the manometer with two gas syringes, which are connected to the bottle via the three-way stopcock (compare Fig. 2). One of the gas syringes is mounted horizontally and the other is positioned vertically with its plunger oriented downwards. While making measurements, the three-way cock must be positioned in such a manner that it only connects the vertical syringe with the bottle. To increase the plunger's mass, a nickel sheet metal electrode is attached to it with two-sided tape. Start the

Fig. 2: Experimental set-up (C_p)



plunger rotating manually before the measurement so that it rotates throughout measurement. In this manner the static friction between the plunger and the body of the syringe is minimised and the measured values are sufficiently exact. If the plunger stops prematurely, the volume increase (ΔV) read on the vertically mounted syringe is too low. Determine the air pressure, which is required for the calculations, with the aid of digital barometers. For the calculations use a value which lies 14 hPa lower as the atmospheric pressure (compare Theory and evaluation) for the pressure in the gas container. In this way the pressure depression due to the mass of the syringe's plunger is taken into consideration.

For the determination of C_p, also perform at least 10 measurements. After each measurement remove air from the system until the vertical syringe again exhibits the initial volume determined in the first measurement. To do this, turn the three-way cock in such a manner that both syringes and the bottle are connected with each other.

Theory and evaluation

The first law of thermodynamics can be illustrated particularly well with an ideal gas. This law describes the relationship between the change in internal intrinsic energy ΔU_i the heat exchanged with the surroundings ΔQ and the constant-pressure change $p\mathrm{d}V$.

$$\mathrm{d}Q = \mathrm{d}U_i + p\mathrm{d}V \tag{1}$$

The molar heat capacity C of a substance results from the amount of absorbed heat and the temperature change per mole:

$$C = \frac{1}{n} \cdot \frac{dQ}{dT} \tag{2}$$

n = number of moles

One differentiates between the molar heat capacity at constant volume C_V and the molar heat capacity at constant pressure C_p.

According to equations (1) and (2) and under isochoric conditions (V const., $\mathrm{d}V = 0$), the following is true:

$$C_V = \frac{1}{n} \cdot \frac{\mathrm{d}U_i}{\mathrm{d}T} \tag{3}$$

and under isobaric conditions (p = const., $\mathrm{d}p = 0$):

$$C_p = \frac{1}{n}\left(\frac{\mathrm{d}U_i}{\mathrm{d}T} + p\frac{\mathrm{d}V}{\mathrm{d}T}\right) \tag{4}$$

Taking the equation of state for ideal gases into consideration:

$$pV = n\,R\,T \tag{5}$$

it follows that the difference between C_p and C_V for ideal gases is equal to the universal gas constant R.

$$C_p - C_V = R \tag{6}$$

It is obvious from equation (3) that the molar heat capacity C_V is a function of the internal intrinsic energy of the gas. The internal energy can be calculated with the aid of the kinetic gas theory from the number of degrees of freedom f:

$$U_i = \frac{1}{2}\,f\,k_B\,N_A\,T\,n \tag{7}$$

where

$k_B = 1.38 \cdot 10^{-23}$ J/K (Boltzmann Constant)
$N_A = 6.02 \cdot 10^{23}\ \mathrm{mol}^{-1}$ (Avogadro's number)

Through substitution of

$$R = k_B\,N_A \tag{8}$$

it follows that

$$C_V = \frac{f}{2}\,R \tag{9}$$

and taking equation (6) into consideration:

$$C_p = \left(\frac{f+2}{2}\right)R \tag{10}$$

The number of degrees of freedom of a molecule is a function of its structure. All particles have 3 degrees of translational freedom. Diatomic molecules have an additional two degrees of rotational freedom around the principal axes of inertia. Triatomic molecules have three degrees of rotational freedom. Air consists primarily of oxygen (approximately 20 %) and nitrogen (circa 80 %). As a first approximation, the following can be assumed to be true for air:

$f = 5$
$C_V = 2.5$ R
$C_V = 20.8\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$

and

$C_p = 3.5$ R
$C_p = 29.1\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$.

Determination of C_p

The energy ΔQ is supplied to the gas by the electrical heater:

$$\Delta Q = U \cdot I \cdot \Delta t \tag{11}$$

where

U = the voltage which is applied to the heater wires (measured separately)
I = the current, which flows through the heater wires (measured separately)
Δt = the period of time in which current flowed through the wires

At constant pressure the temperature increase ΔT induces a volume increase ΔV From the equation of state for ideal gases, it follows that:

$$\Delta V = \frac{nR}{p}\,\Delta T = \frac{V}{T}\,\Delta T \tag{12}$$

and taking equation (2) into consideration, the following results from equations (11) and (12):

$$C_p = \frac{1}{n} \cdot \frac{U \cdot I \cdot \Delta t \cdot V}{\Delta V \cdot T} \tag{13}$$

The molar volume of a gas at standard pressure p_0= 1013 hPa and T_0 = 273.2K is:

$$V_0 = 22.414 \text{ l/mol.}$$

The molar volume is:

$$V_{\text{mol}} = \frac{p_0 V_0}{T_0} \frac{T}{p} \tag{14}$$

In accordance with the following, the number of moles in volume V is:

$$n = \frac{V}{V_{mol}} \tag{15}$$

C_p can be calculated using equation (13) under consideration of (14) and (15):

$$C_p = \frac{p_0 V_0}{T_0} \cdot \frac{U\,I}{p} \cdot \frac{\Delta t}{\Delta V} \tag{16}$$

The pressure p used in equation (16) is calculated from the atmospheric pressure minus the pressure reduction due to the weight of the syringe's plunger. The pressure reduction is calculated from:

$$p_K = \frac{m_K \cdot g}{F_K}$$

$$= \frac{0.1139 \text{ kg} \cdot 9.81 \text{ ms}^{-2}}{7.55 \cdot 10^{-4} \text{ m}^2}$$

$$= 1480 \text{ kg m}^{-1} \text{ s}^{-1} = 14.8 \text{ hPa}$$

$$p = p_a - p_K$$

$$= 975 \text{ hPa} - 14.8 \text{ hPa}$$

$$= 960 \text{ hPa}$$

where

p = the atmospheric pressure minus the pressure reduction due to the weight of the syringe's plunger

p_K = the pressure reduction due to the weight of the plunger

p_a = measured atmospheric pressure

m_K = 0.1139 kg = mass of the plunger

g = 9.81 m · s^{-2} = acceleration of gravity

F_K = 7.55 · 10^{-4} m^2 = area of the plunger

The slope of the straight line in Fig. 4 is equal to

$$\frac{\Delta V}{\Delta t} = 3.8 \frac{ml}{s}$$

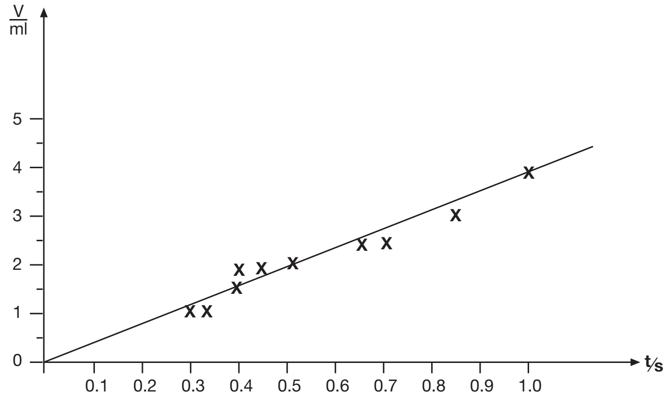
with

U = 4.7 V and I = 0.31 A

C_p is obtained with equation (16)

C_p = 33 J · K^{-1} · mol^{-1}

Fig. 4: Volume change ΔV as a function of the heat-up time Δt. U = 4.70 V, I = 0.31 A.



Determination of C_V

Under isochoric conditions, the temperature increase ΔT produces a pressure increase Δp. The pressure measurement results in a minute alteration of the volume which must be taken into consideration in the calculation:

$$\Delta T = \frac{p}{nR}\,\Delta V + \frac{V}{nR}\,\Delta p = \frac{T}{pV}\,(p\Delta V + V\Delta p) \tag{17}$$

It follows from equations (3) and (1) that:

$$C_V = \frac{1}{n} \cdot \frac{\Delta Q - p\Delta V}{\Delta T} \tag{18}$$

and with equations (11) and (17) one obtains:

$$C = \frac{p \cdot V}{n \cdot T} \cdot \frac{U \cdot I\Delta t - p\Delta V}{p\Delta V + V\Delta p} \tag{19}$$

The indicator tube in the manometer has a radius of r = 2 mm. A pressure change of p = 0.147 hPa causes an alteration of 1 cm in length; the corresponding change in volume is therefore:

$$\Delta V = a \cdot \Delta p \tag{20}$$

where

$$a = \pi r^2 \cdot \frac{1}{0.147} \cdot \frac{\text{cm}}{\text{hPa}} = 0.855 \frac{\text{cm}^3}{\text{hPa}} \tag{21}$$

thus

$$C_V = \frac{p\,V U \cdot I\,\Delta t - a\,p \cdot \Delta p}{nT \cdot (a\,p + V) \cdot \Delta p} \tag{22}$$

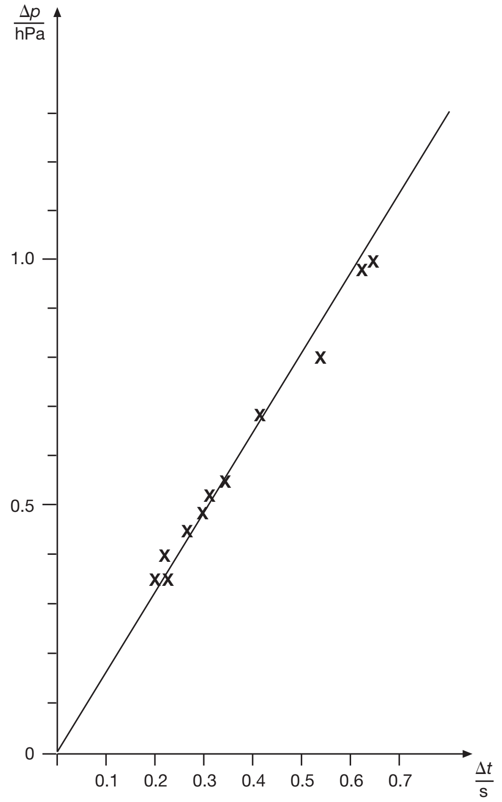
Taking equations (14) and (15) into consideration, it follows that:

$$C_V = \frac{p_0 V_0}{T_0} \cdot \left(\frac{U \cdot I\Delta t}{(a\,p + V) \cdot \Delta p} - \frac{a\,p}{a\,p + V}\right) \tag{23}$$

The slope of the straight line in Fig. 5 is equal to

$$\frac{\Delta p}{\Delta t} = 167 \frac{Pa}{s}$$

Fig. 5: Pressure change Δp as a function of the heat-up time Δt. U = 4.75 V, I = 0.25 A



C_v can be calculated using equation (23) if equation (21) is taken into consideration.

With the atmospheric pressure

$$p = 1011 \text{ hPa}$$

(this part of the experiment was done on another day), a volume of

$$V = 1.14 \text{ l}$$

$$U = 4.75 \text{ and } I = 0.25 \text{ A}$$

the following value for C_V is obtained:

$$C_V = 26 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}.$$

As a consequence of heat losses to the surroundings, the experimentally determined values for C_p and C_V are somewhat larger than the theoretical ones. The difference between the molar heat capacities provides the value for R.

The experiment results give

$$R = C_p - C_v$$

$$= 7 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

Value taken from literature:

$$R = 8.3 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

Note

Using this apparatus, other gases (e.g. carbon dioxide or argon) can also be measured. These gases are then introduced through the stopcock on the bottom of the vessel.

Data and Results

Literature values:

$$C_{p(\text{oxygen})} = 29.4 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$C_{V(\text{oxygen})} = 21.1 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$C_{p(\text{nitrogen})} = 29.1 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$C_{V(\text{nitrogen})} = 20.8 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$R = 8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$= 83.14 \text{ hPa} \cdot \text{l} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

Experimental results:

$$C_p \text{ (air)} = 33 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$C_v \text{ (air)} = 26 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$