Temperature and Heat

Introduction: In the scientific analysis it is essential to clearly identify the subject matter of analysis on which we focus our attention. For this purpose, we use identify an important terms that are used in the following chapters**.** We define the **system** as a quantity of matter bounded by some surface which separates it from the rest of the world. It can be anything, e.g. a beaker filled by liquid or a piece of magnet or any other complex components.

$$\underbrace{\boxed{\boxed{\text{Matter}}}}_{\text{System}}$$

$$\left(\text{Matter} + \text{Boundary}\right) \equiv \text{System}$$

The system could be studied in two different approaches:

1- **Thermodynamics**: is concerned with the **gross** (**macroscopic**) features of the system. **Pressure** "P", **volume** "V", and **temperature** "T" are the most important **macroscopic variables (coordinates** which defined the **state** of a system**)**. The equation that contains the macroscopic variables, e.g. the ideal gas law $PV = nRT$, is called **equation of state**.

2- **Statistical Mechanics**: deals with a system containing a large number of particles and its **microscopic** properties, e.g. **speeds**, **energies**, **masses**, etc. For a very large number of particles, averages of these particle properties are considered.

If the system is not completely isolated, it could interact with the external space or matter which called **surrounding (environment)**. The combination of the $\left(\text{system} + \text{surrounding}\right)$ define the **Universe.**

Temperature: is a fundamental physical concept as the three fundamental quantities of mechanics - mass, length, and time. It is familiar as the property of a body of matter responsible for sensations of **hot** or **cold** when it is touched. It depends on the average kinetic energy of the particles in the matter (see the kinetic theory of gasses). The temperature of a body is usually measured by a thermometer (e.g. thermocouple, constant-volume gas, etc.)

Important Note:

- We are going to deal with equilibrium situations, those situations in which a temperature may be well defined, i.e. **thermal equilibrium** situation. In thermal equilibrium, we mean that all parts of the system are at the same temperature as that of the relevant environment. Simply, **Thermal equilibrium** ≡ **same temperature**.

Ideal Gas

In the following we will consider a sample of gas molecules; we will call it system, which has the following properties (see Figure 1):

•	$\boxed{\boxed{N_A, \quad M = mN_A}}$	$\boxed{\boxed{N, \quad M_{\text{sample}} = Nm = nM, \quad n = \dfrac{N}{N_A}}}$
m	1 mole	Sample

Figure (1)

For one particle (molecule):

m = molecular mass (mass of one molecule)
For one mole, we have:
N_A = the Avogadro's number.
$M = m\,N_A$ = molar mass (mass of one mole).
For the sample, we have:
N = number of molecules in the sample.
M_{sample} (in kg) = mass of the sample $= N\,m$

Examples: For O_2; M = 32 g/mol, and for H_2 is M = 2 g/mol.

Ideal (perfect) Gas Law: Consider a sample of n moles (or N molecules) of gas contained in a volume V and at absolute temperature T and pressure P. The empirical relation between P, V, and the absolute temperature T is given by the relation:

$$P\,V = n\,R\,T = N\,k\,T,$$

where R is the universal gas constant = 8.314 J/(mol.K), $[P]$ = N/m² = Pascal, $[V]$ = m³, and $[T]$ = K. If the sample volume contains M_{sample} kg of gas that has a molar mass M (= the mass of 1 mol of that substance), then

$$n = \frac{M_{sample}}{M} = \frac{M_{sample}}{mN_A} = \frac{mN}{mN_A} = \frac{N}{N_A}.$$

where $k = R/N_A = 1.38\times10^{-23}$ J/K is the Boltzmann's constant..
Avogadro's number: is the number of particles (or atoms or molecules) in 1 mole, and is the same for all substances. $N_A = 6.023\times10^{23}$ particles/mole,

Mass of an atom or molecule, $m = \dfrac{M}{N_A}$.

Comments:

I. The ideal gas is held at low density.
II. The temperature (T) always measured in K, not in °C or °F.
III. $1\ \text{atm.L} = 1.013\times10^5\ \dfrac{\text{N}}{\text{m}^2}\times10^{-3}\ \text{m}^3 = 101.3\ \text{N.m} = 101.3\ \text{J}.$
IV. The real gas behaves more like an ideal gas at low pressure and high temperature.

➔ The molecular weight (M) of O_2 is 32 g/mol, therefore, 32 g of O_2 contains N_A molecules and ½ mole has a mass of 16 g.

➔ Gold has a molar mass of 197 g/mole.

a) How many moles of gold in a 2.5 g sample of pure gold?

✓ $$n = \frac{M_{sample}}{M} = \frac{2.5\ \text{g}}{197\ \text{g/mole}} = 0.013\ \text{mole}.$$

b) How many atoms are in the sample?

✓ $$N = nN_A = 7.6\times10^{21}\ \text{atoms}.$$

➔ How many hydrogen atoms and how many oxygen atoms are in an ice cube of mass 8 grams?

✓ The molecular weight of H_2O is (2×1+16) = 18. Thus 8 grams of H_2O is 8/18 = 0.44 mole. One mole has N_A molecules, so 0.44 mole has $(0.44 \times N_A) = 2.68 \times 10^{23}$ molecules. In each H_2O there is one oxygen atom and two hydrogen atoms, so in 8 grams of ice cube there are 2.68×10^{23} oxygens and 5.36×10^{23} hydrogen.

Absolute Zero: is unique temperature at which P and V reach zero.

Standard Condition (Standard Temperature and Pressure) S.T.P. is defined to be:

$$T = 273.15 \text{ K} = 0\ ^{o}\text{C}, \qquad P = 1.013 \times 10^5 \frac{\text{N}}{\text{m}^2} (\text{or Pa}) = 1 \text{ atm}$$

➔ Show that one mole of any gas at S.T.P. occupies a volume of 22.4 L.

✓ $$V = \frac{n\,R\,T}{P} = \frac{(1 \text{ mol})(8.314 \frac{\text{J}}{\text{mol.K}})(273.15 \text{ K})}{(1.013 \times 10^5 \frac{\text{N}}{\text{m}^2})} = 22.4 \times 10^{-3} \text{ m}^3 = 22.4 \text{ L}$$

➔ Find the density of ammonia, NH_3,

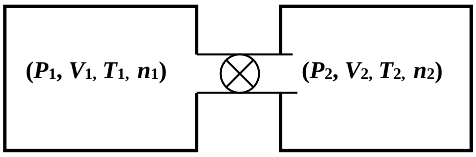
✓ At STP one mole of any gas occupies 22.4 L. The molecular mass of NH_3 is:

$$1\text{N} = 1 \times 14.01 \text{ u} = 14.01 \text{ u}$$
$$3\text{H} = 3 \times 1.008 \text{ u} = \underline{3.02 \text{ u}}$$
$$17.03 \text{ u} = 17.03 \text{ g/mole}$$

One mole of NH_3, therefore, has a mass of 17.03 g at STP, and its density is:

$$\rho = \frac{m}{V} = \frac{17.03 \text{ g}}{22.4 \text{ L}} = 0.76 \text{ g/L} = 0.76 \text{ kg/m}^3.$$

➔ Consider two thermally insulated vessels connected by a short tube with a valve. Both the vessel are filled with ideal gas having volume (P_1, V_1, T_1, n_1) and (P_2, V_2, T_2, n_2), as shown in the figure. If the valve is opened, find the final pressure and temperature of gas.



✓ Before opening the valve the ideal gas law gives,

$$P_1V_1 = n_1RT_1, \quad P_2V_2 = n_2RT_2,$$

After connection and at equilibrium, the final pressure "P" will be the same, so the ideal gas law gives,

$$P(V_1 + V_2) = R(n_1T_1 + n_2T_2)$$
$$= P_1V_1 + P_2V_2$$

This means: $P = \dfrac{P_1V_1 + P_2V_2}{(V_1 + V_2)}$

➔ The density of air at 0 ^{o}C and 1 atm pressure is 1.293 kg/m³. Find its density at 100 ^{o}C and 2 atm pressure?

✓ The given data are:

$$P_i = 1.01\times 10^5 \text{ Pa},\quad P_f = 2.02\times 10^5 \text{ Pa},\quad T_i = 273 \text{ K},\quad T_f = 373 \text{ K}.$$

Use the ideal gas law as a ratio: $\frac{P_i V_i}{T_i} = \frac{P_f V_f}{T_f}$, $V_j = \frac{\text{m}}{\rho_\text{j}}$., one can find

$$\rho_f = \rho_i \frac{P_f T_i}{P_i T_f} = 1.293\frac{2(273)}{1(373)} = 1.893 \text{ kg/m}^3.$$

➔ a- A spherical balloon of radius 0.80 m is filled with an ideal gas and located in a region where the pressure is 3.0×10^5 Pa and the temperature is 12 °C. Assume the balloon has the same pressure and temperature as its surroundings. Find the number of moles of ideal gas in the balloon. [$V=(4/3)\pi r^3=2.14$ m^3]

✓ $$n = \frac{PV}{RT} = \frac{(3.0\times10^5 \text{ N/m}^2)(2.14 \text{ m}^3)}{(8.314 \text{ J/K})(285 \text{ K})} = 272 \text{ moles}.$$

b- The balloon in part (a) is moved to another region where the pressure is 1.5×10^5 Pa. When the balloon reaches the same pressure and temperature as this new region, its radius is found to increase by 0.22 m. What must the temperature of this region be in °C?

✓ $$T_f = \frac{P_f V_f}{nR} = \frac{(1.5\times10^5 \text{ N/m}^2)\frac{4}{3\pi}(0.80{+}0.22)^3}{(8.314 \text{ J/K})(285 \text{ K})} = 295 \text{ K} = 22\ {}^\circ\text{C}.$$

True-False Questions

1- In using the Ideal gas law it is necessary that temperature be expressed in $^\circ$C. F
2- One mole of gas contains 6×10^{23} molecules only if the gas is a monatomic gas. F
3- When making calculations with the ideal gas law, pressure must be expressed in atmospheres. F
4- When heat is added to a gas its temperature will raise by an amount independent of whether or not the pressure or volume is held constant. F (latent heat)
5- A real gas behaves more like an ideal gas at high temperatures than at low temperatures. T
6- For the same increase in temperature, solids generally expand less than liquids. T
7- The number of molecules (N), the universal gas constant (R) and the absolute temperature (T) are all thermodynamic variables. F
8- As the temperature increases from zero $^\circ$C to 4 $^\circ$C, the water's density increases. T
9- Water, ice and water vapor can coexist in equilibrium. T
10- If the average kinetic energy of the molecules in a solid increases, this means the temperature increases. T

First Law of Thermodynamics

What is thermodynamics? It is the field of physics that studies the properties of systems that have a temperature and involve the laws that govern the conversion of energy from one form to another, the direction in which heat will flow, and the availability of energy to do work.

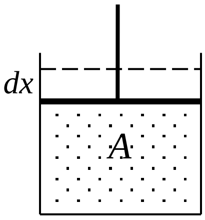
Work: (W, [W] = J) A system (e.g. gas in cylinder of a tight frictionless piston) may exchange energy with its surroundings through work. In a process, the total work done "W" by a system as it changes from an initial volume V_i to a final volume V_f in any process is given by:

$$W = \int_{V_i}^{V_f} P dV$$

The integration is necessary because the pressure P may be vary during the process. At constant pressure,

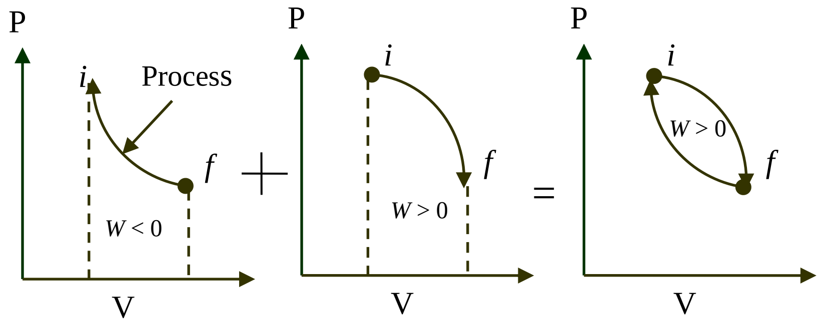
$$W = \int_{V_i}^{V_f} P dV = P \Delta V = \begin{cases} \Delta V > 0 \Rightarrow W = \text{positive} \Rightarrow \text{ work done by the system} \\ \Delta V < 0 \Rightarrow W = \text{negative} \Rightarrow \text{ work done on the system} \end{cases}$$

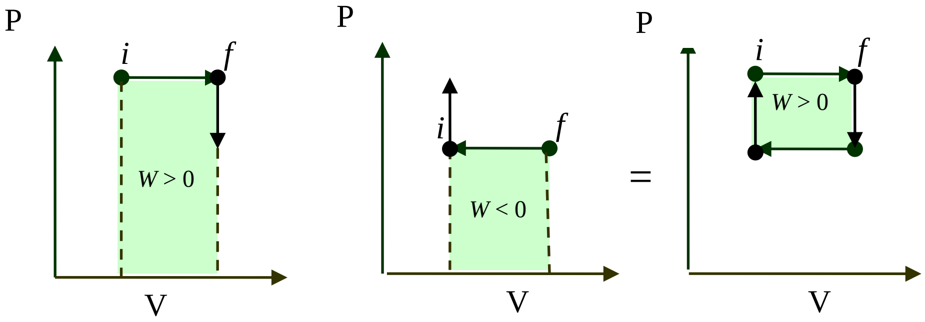
The total work done in any process and the total work is the area under the curve in *PV*-diagram]



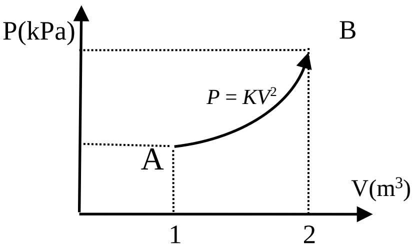
[**Proof**: Consider an ideal gas confined to a cylinder of a tight frictionless piston, see above figure. Let V = volume of the enclosed gas, P = pressure of the gas. If the gas expands moving the piston dx, so the change in volume $dV = Adx$, where A is the area of the piston. The force exerted by the gas on the piston $F = PA$ and the work done is $dW=Fdx=PAdx=PdV$.

➔





➔ A sample of an ideal gas is expanded to twice of its original volume of $1.0\ \mathrm{m}^3$ in a quasi-static process for which $P = KV^2$ where K is a constant whose value is 5.0 Pa/m^6, as shown in the figure. Calculate the work done by the gas.



✓

$$W = \int_{V_i}^{V_f} P\,dV = K\int_{1}^{2} V^2 dV = K\left.\frac{V^3}{3}\right|_{1}^{2} = \frac{7}{3}K \approx 11.7\ \text{J.}$$

The Internal Energy (U) of a system is the total energy content of the system. It is the sum of the kinetic, potential, chemical, electrical, and all other forms of energy possessed by the atoms and molecules of the system. U is path independent, but Q and W are path dependent. *For an **ideal gas**, the internal energy depends only on **temperature**.*

First Law of Thermodynamics is an energy conservation statement. It states that "*if an amount of heat energy, ΔQ, flows into a system, then this energy must appear as increased internal energy, ΔU, for the system and/or work, ΔW, done by the system on its surrounding*". In symbols

$$\Delta Q = \Delta U + \Delta W$$

ΔU is independent of the path over which the change from i to f is carried out. The quantities ΔQ and ΔW in general depend on the path.

Sign convention: The convention is adopted that Q indicates the heat added to the system and W the work done by it. Thus,

$dQ > 0$, heat added (entered) to system (or system absorbs (gains) heat).

$dQ < 0$, heat removed from system (or system rejects (loses) heat).

$dW > 0$, work is done by system.

$dW < 0$, work is done on the system.

$dU > 0$, internal energy of system increases.

$dU < 0$, internal energy of system decreases.

Another definition of Heat: it is the change in internal energy of a system when no work is done on (or by) the system.

Table: Summary of the most common processes.

Process	Definition	Restrictions	Work done by the gas	Consequences
Free expansion	isolated	$\Delta Q = 0$ $\Delta U = 0$ $\Delta W = 0$	$\Delta W = 0$	0
Cyclic process	closed	$\Delta U = 0$	$\Delta W = \Delta Q$	ΔQ
Adiabatic	no heat exchange	$\Delta Q = 0$	Area under the curve	$\Delta W = -\Delta U$
Isobaric $P =$ constant	no change in pressure	$\Delta P = 0$	$P\Delta V$	$\Delta W = P\Delta V$
Isochoric (Isovolumic) $V =$ constant	no change in volume	$\Delta V = 0$	Zero	$\Delta Q = \Delta U$
Isothermal $T =$ constant,	no change in temperature	$\Delta T = 0$, $\Delta U = 0$	Area under the curve	$= nRT \ln(\frac{V_f}{V_i})$ $= nRT \ln(\frac{P_i}{P_f})$

➔ Determine the change in the internal energy of a system that:

a- absorbs 500 cal of thermal energy while doing 800 J of external work.

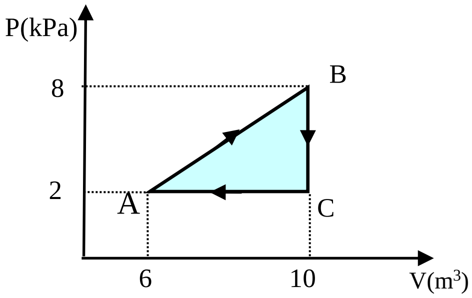
✓
$$\begin{aligned}\Delta U &= \Delta Q - \Delta W \\ &= 500\times 4.186 - 800 = 1290 \text{ J.}\end{aligned}$$

b- absorbs 500 cal of thermal energy while doing 800 J of external work is done on the system.

✓
$$\begin{aligned}\Delta U &= \Delta Q - \Delta W \\ &= 500\times 4.186 + 800 = 2893 \text{ J.}\end{aligned}$$

c- is maintained at a constant volume while 1000 cal is removed from the system.

✓
$$\begin{aligned}\Delta U &= \Delta Q - \Delta W \\ &= -1000\times 4.186 + 0 = -4186 \text{ J.}\end{aligned}$$



➔ A gas is taken through the cyclic process described in the above figure.

a- Find the net heat transferred to the system during one complete cycle.

✓ For the cyclic processes

$$\Delta U = 0, \quad \Rightarrow \quad \text{Q(ABCA)} = \text{W(ABCA)}$$

$$\begin{aligned}Q(\text{ABCA}) &= \text{Area of triangle} \\ &= \tfrac{1}{2}\,(10-6)\text{m}^3(8-2)\text{kPa} = 12.0 \text{ kJ}\end{aligned}$$

this means that the system (gas) gains heat.

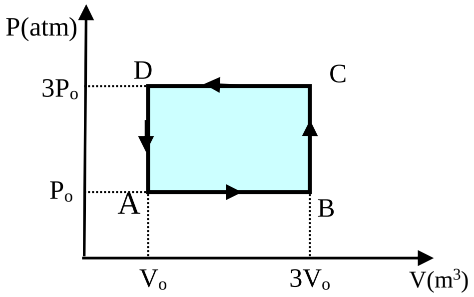
b- If the cycle is reversed, that is, the process goes along ACBA, what is the net heat transferred per cycle?

✓ In the reversible process

$$Q(\text{ACBA}) = -Q(\text{ABCA}) = -12.0 \text{ kJ.}$$

So, the system expels heat.

➔ One mole of an ideal gas is taken along the cyclic path A→B→C→D→A.



a- What is ΔU for the cycle?

✓ $\Delta U = 0$ for the cyclic process.

b- Find the net work done by the gas per cycle.

✓
$$W(AB) = P\Delta V = P(V_f - V_i) = P_o(3V_o - V_o) = 2\ P_oV_o$$
$$W(BC) = W(DA) = 0\,,$$
$$W(CD) = P\Delta V = P(V_f - V_i) = P_o(V_o - 3V_o) = -6\ P_oV_o$$

Then the net work done on the system is:

$$\Delta W = W(AB) + W(BC) + W(CD) = -4\ P_oV_o$$

c- What is ΔQ for the cycle?

✓
$$\Delta Q = \Delta W = -4P_oV_o$$

d- Is the heat added to the gas or expelled from it? Explain your choice.

✓ The net heat is expelled from the system because ΔQ is negative.

Note that:

$$Q\,(\text{ABCDA}) = \text{Area of rectangle}$$
$$= (V_o - 3V_o)m^3(3P_o - P_o) = -4\ V_oP_o$$

➔ Helium gas is heated at constant pressure from 32 ^{o}F to 212 ^{o}F. If the gas does 20.0 Joules of work during the process, what is the number of moles?

✓
$$W = P\Delta V = nR\Delta T$$
$$\Rightarrow \quad n = \frac{W}{R\Delta T} = \frac{20}{8.314\times\frac{5}{9}(212-32)} = 0.024 \text{ mole.}$$

Work done in Isothermal Expansion: The work done by an ideal gas during an Isothermal (constant temperature) change from initial state (P_i , V_i) to final state (P_f , V_f) is calculated as:

$$W = \int_{V_i}^{V_f} PdV = nRT \int_{V_i}^{V_f} \frac{dV}{V} = nRT \ln(\frac{V_f}{V_i}) = nRT \ln(\frac{P_i}{P_f})$$

Comments:

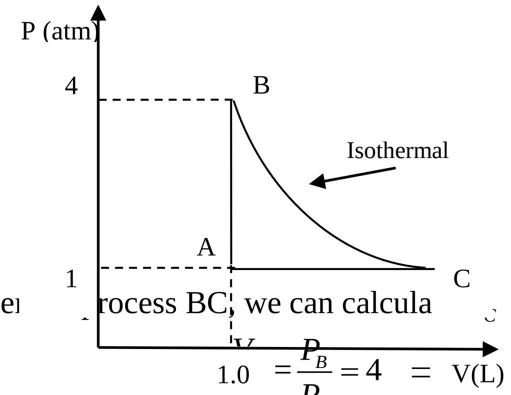
Many other relations may be used, for example by changing $nRT \rightarrow P_i V_i = P_f V_f$.

- ➔ One mole of an ideal gas compressed at constant temperature of 310 K from an initial volume of 19 L to a final volume of 12 L.
  a) How much work is done by the compressing gas?

✓ $$W = nRT \ln(\frac{V_f}{V_i}) = (1)(8.314)(310)\ln(\frac{12}{19}) = -1180 \text{ J.}$$

The negative sign means that work is done on the system.

- ➔ Four moles of an ideal gas undergoes the thermodynamic process shown in the figure. If the process BC is an isothermal, how much work is done by the gas in this cyclic process?



✓ In the isothe rocess BC, we can calcula as:

$$= \frac{P_B}{P_C} = 4 \quad = \quad 4 \text{ L.}$$

and the total work done is:

$$W_{total} = W_{AB} + W_{BC} + W_{CA},$$

where

$$W_{AB} = 0 \text{ (isochoric process),}$$

$$\begin{aligned} W_{CA} &= P_A(V_A - V_C) \\ &= (1\times1.01\times10^5)(1.0\times10^{-3} - 4.0\times10^{-3}) \\ &= -3.0\times10^2 \text{ J,} \end{aligned}$$

$$\begin{aligned} W_{BC} &= nRT_B \ln(\frac{V_C}{V_B}) = P_B V_B \ln(\frac{V_C}{V_B}) \\ &= (4\times1.01\times10^5)(1.0\times10^{-3})\ln 4 \\ &= 5.60\times10^2 \text{ J} \end{aligned}$$

so the total work done will be: $$\begin{aligned} W_{total} &= W_{AB} + W_{BC} + W_{CA} \\ &= 0 - 3.0\times10^2 + 5.6\times10^2 = \underline{2.6\times10^2 \text{J}}. \end{aligned}$$

The positive work done means its done by the gas.

Specific heat for gases: Consider the expansion of an ideal gas at constant volume (i.e. $\Delta V = \Delta W = 0$), if we define c_v as the molar specific heat at constant volume, then

$$\Delta Q = \Delta U = nc_v \Delta T$$

If we considered the expansion at constant pressure and using the first law of thermodynamics, then

$$\Delta Q = \Delta U + \Delta W = nc_v \Delta T + nR\Delta T = nc_p \Delta T, \qquad c_p = c_v + R$$

where c_p is the molar specific heat at constant pressure.

For **monatomic** ideal gases (consisting of a single atom, e.g. He, Ar), $c_v = \frac{3}{2}R$.

For **diatomic** ideal gases (consisting of two atoms, e.g. H_2, O_2, air), $c_v = \frac{5}{2}R$.

Notes:

1. The above expressions applied for ideal gas only.
2. ΔU is a function of temperature only and has the same expression in all processes.

➔ In a constant-volume process, 209 J of heat is added to 1 mole of an ideal monatomic gas initially at 300 K. Find the final temperature of the gas.

✓ Using the first law of thermodynamics:

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

with our condition at constant volume, i.e.

$$\Delta V = 0, \quad \Delta U = \Delta Q = 209 \text{ J.}$$

One can calculate

$$\Delta Q = \Delta U = nc_v \Delta T = n(\frac{3}{2}R)\Delta T = 209 \text{ J}$$

$$\Rightarrow \quad \Delta T = \frac{2\times 209}{3\times 8.314\times 1} = 16.8 \text{ K.}$$

and the final temperature will be

$$\therefore\ T_f = T_i + \Delta T = (300+16.8) \text{ K} \approx 317 \text{ K.}$$

➔ Two moles of helium (monatomic) gas are heated from 100 °C to 250 °C. How much heat is transferred to the gas if the process is isobaric?

✓ $$\Delta Q = nc_p \Delta T = 2(\frac{5}{2}8.314)(250-100) = 6.23\times 10^3 \text{ J.}$$

➔ Two moles of helium (monatomic) gas are heated from 0.0 °C to 100 °C. How much heat is transferred to the gas if the process is isochoric?

✓ $$\Delta Q = \Delta U = nc_v \Delta T = 2(\frac{3}{2}\times 8.31)(100-0.0) = 2.49\times 10^3 \text{ J.}$$

➔ Two moles of helium (monatomic) gas are initially at a temperature of 27 °C and occupy a volume of 20 liters. The helium is expanded at constant pressure until the volume is doubled. [Note thet

$$\frac{V_i}{T_i}=\frac{V_f}{T_f} \quad \Rightarrow \quad T_f = T_i\left(\frac{V_f}{T_f}\right)=600\text{ K.}]$$

a- Find the total heat supplied in the process,

✓ $$Q = nc_p\Delta T \ = nc_p(T_f - T_i)\text{=}2(\frac{5}{2}\text{R})(300)\text{=}1.25\times10^4 \text{ J.}$$

b- Find the change in the internal energy,

✓ $$Q = nc_v\Delta T \ = nc_v(T_f - T_i)\text{=}2(\frac{3}{2}\text{R})(300)\text{=}7.48\times10^3 \text{ J.}$$

c- Find the work done by the system.

✓ $$W = Q - U = 1.25\times10^4 - 7.48\times10^3 = 5.02\times10^3 \text{ Joules.}$$

In quasi-static, **adiabatic expansion** (i.e. ΔQ = 0) one gets

$$PV^\gamma = \text{ constant,} \quad \Rightarrow \quad P_iV_i^\gamma = P_fV_f^\gamma, \qquad \gamma = \frac{c_p}{c_v}$$

Using the ideal gas law, one gets

$$T_iV_i^{\gamma-1} = T_fV_f^{\gamma-1}, \qquad T_iP_i^{\frac{1-\gamma}{\gamma}} = T_fP_f^{\frac{1-\gamma}{\gamma}},$$

➔ An ideal diatomic gas ($c_v = 3/2, c_p = 5/2$), initially at a pressure P_i=1.0 atm and the initial volume V_i, is allowed to expand isothermally until its volume doubles. The gas is then compressed adiabatically until it reaches its original volume. The final pressure of the gas will be:

✓ We are giving P_i=1.0 atm, V_f=2V_i and $P_i=\frac{1}{2}$ atm, consequently:

$$P_f = P_i\left(\frac{V_f}{V_i}\right)^\gamma = (\frac{1}{2})(2)^{1.4} = 1.3\text{ atm.}$$

➔ Two moles of an ideal gas (γ = 1.40) expand quasi-statically and adiabatically from a pressure of 5 atm and a volume of 12 liters to a final volume of 30 liters.

a-What is the final pressure of the gas?

✓ $$P_2 = P_1\left(\frac{V_1}{V_2}\right)^\gamma = (5\text{ atm})\left(\frac{12}{30}\right)^\gamma = 1.39\text{ atm.}$$

b- What are the initial and final temperatures?

✓ $$T_i = \frac{P_1V_1}{nR} = \left(\frac{(5.00)(1.01\times10^5)(12\times10^{-3})}{2(8.314)}\right) = 364.6\text{ K},$$

$$T_f = \frac{P_2V_2}{nR} = \left(\frac{(1.39)(1.01\times10^5)(30\times10^{-3})}{2(8.314)}\right) = 253.4\text{ K.}$$

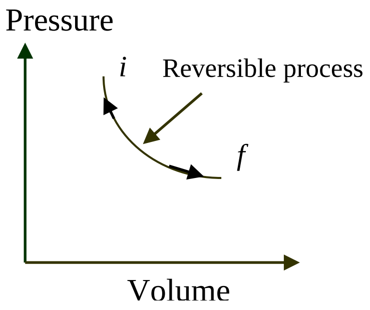
True-False Questions

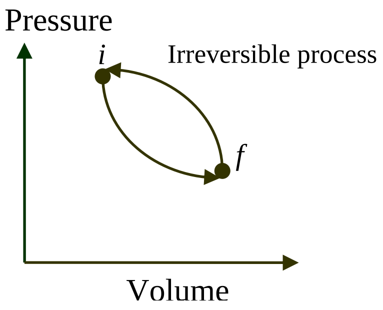
1- For the ideal gas $C_p - C_V = R/2$. F
2- In an isothermal process, there is no change in the internal energy. T
3- In an adiabatic process, no heat enters or leaves the system. T
4- In an isochoric process, the work done by the system is positive. F
5- In an isothermal process, the work done is equal to heat energy. T
6- In any cyclic process, the work done by the gas is zero. F
7- The first law of thermodynamics represents the conservation of energy. T
8- The internal energy of a system is a state function. T
9- In an isobaric process, the change in internal energy is always zero. F

Second Law of Thermodynamics

The first law of thermodynamics is an energy conservation statement. It determines whether or not a process can take place energetically. It does not tell in which direction the process can go, even that they are energetically possible. For examples: A rock will fall if you lift it up and then let go, and never come back to your hand by itself. Hot frying pans loose heat and cool down when taken off the stove. Air in a high-pressure tire leaks out from even a small hole in its side to the lower pressure atmosphere, and never sees the reverse process. Ice cubes gains heat and melt in a warm room. Second law of thermodynamics is based on human experience. It doesn't come from complicated theory and equations and will tell you why some process will be forbidden although they are energetically possible. This is why we have to define the reversibility and irreversibility of a process.

- A **reversible** change (or process) is one in which the values of P, V, T, and U are well defined during the change. If the process is reversed, then P, V, T, and U will take on the same values in reverse order. To be reversible, a process must usually be slow (quasi-statically), and the system must be close to equilibrium during the entire change.
- A process is **irreversible** if the system and its surroundings can not be returned to their initial states, which is the common case in nature.





Second law of Thermodynamics: Many equivalent statements could be specified for the second law of thermodynamics. One of them, due to Claussius and states

"*Heat can not be transferred from a cold reservoir to a warm one without doing work*",

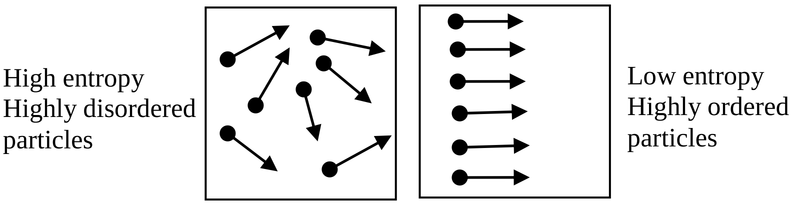
or in another words

"*heat will not flow spontaneously from a colder to a hotter temperature*".

See the animation:

http://www.colorado.edu/physics/2000/bec/what_is_it.html

Entropy (S, $[S]$ = J/K) is a quantity used to measure the degree of **disorder (or randomness)** of a system. Irreversible processes such as spontaneous flow of heat from a hotter to a colder body without the production of useful work always increase the entropy of an isolated system and of the universe.



1. It is a state function of the system like pressure, volume, temperature and energy), i.e. it depend only on the initial and final state of a system and not on how it reach that states That is, a system has definite entropy just as it has a definite internal energy U.

2. The entropy of a system increases when heat flows into the system and decreases when heat flows out.
3. When heat dQ_r enters (or removed from) a system at absolute temperature T, the change in entropy, dS, is defined by the ratio

$$\boxed{dS \equiv \frac{|dQ_r|}{T}}$$

provided the system changes in a reversible way. The change in entropy of a system moving reversible between two equilibrium states *i* and *f* is given by:

$$\Delta S = \int_i^f dS = \underset{\substack{\text{arbitrary}\\\text{reversible}\\\text{path}}}{\int_i^f} \frac{dQ_r}{T} = S_f - S_i$$

This implies that for an irreversible processes between equilibrium states *i* and *f*, the entropy change is evaluated using the last equation, and any convenient reversible path which connects *i* to *f*; the result is of course path dependent.
For thermodynamic processes**:**

$$\Delta \mathrm{S}_{\text{system}} + \Delta \mathrm{S}_{\text{surrounding}} \equiv \Delta \mathrm{S}_{\text{universe}}$$

and the second law of thermodynamics is formulated as the principle of increasing of entropy. This is:

$$\boxed{\Delta \mathrm{S}_{\text{universe}} \geq 0}$$

where the equality applies to reversible process only. For natural process (irreversible) processes one can say"

"*Natural processes starting in an equilibrium state and ending in another proceed in such a direction the entropy of the universe increases*"

Cyclic (dU = 0)

$$\boxed{\Delta S = \oint_i^f \frac{dQ_r}{T} = 0} \qquad \text{(Claussius' theorem)}$$

Adiabatic (dQ = 0)

$$dQ = 0 \qquad \Rightarrow \qquad \boxed{\Delta S = \int_i^f \frac{dQ_r}{T} = 0}$$

Changing Phase (dT = 0 but T = constant)

$$dQ = mL_v\,(or\ \ mL_f) \quad \Rightarrow \quad \boxed{\Delta S = \frac{dQ}{T}}.$$

Same Phase (e.g. **liquid**)

$$dQ = mc\Delta T \quad \Rightarrow \quad \boxed{\Delta S = mc\int_i^f \frac{dT}{T} = mc\ \ln(\frac{T_f}{T_i})}$$

Same Phase (e.g. **gases**)

$$dQ = \begin{cases} nc_p \Delta T \quad \Rightarrow \Delta S = \boxed{nc_p \int_i^f \frac{dT}{T} = nc_p \ln(\frac{T_f}{T_i})} & \text{(constant pressure)} \\ nc_v \Delta T \quad \Rightarrow \Delta S = \boxed{nc_v \int_i^f \frac{dT}{T} = nc_v \ln(\frac{T_f}{T_i})} & \text{(constant volume)} \end{cases}$$

Isothermal process ($\Delta U = \Delta T = 0$) hence

$$dQ = dW = P\Delta V = nRT \frac{\Delta V}{V} \quad \Rightarrow \quad \boxed{\Delta S = nR \int_i^f \frac{dV}{V} = nR \ln(\frac{V_f}{V_i})}$$

Heat transfer between two masses defined as (m_1,c_1,T_1) and (m_2,c_2,T_2)

$$\Delta S = m_1 c_1 \ln(\frac{T_f}{T_1}) + m_2 c_2 \ln(\frac{T_f}{T_2})$$

where T_f is the equilibrium temperature.

➔ How much does the entropy increase in the following cases?

a) 18-gram ice cube at 0 °C is changed to water at 0 °C . [$L_f = 3.33\times10^5$ J/kg]

✓ $$dS_1 \equiv \frac{dQ_r}{T} = \frac{mL_f}{T} = \frac{0.018\times(3.33\times10^5)}{273+0} = \underline{22.0 \text{ J/K}}$$

b) 18-gram of water at 0 °C is changed to water at 100 °C . [c(water) = 4186 J/(kg.K)]

✓ $$dS_2 = mc\ln(\frac{T_f}{T_i}) = 0.018\times4186\times\ln(\frac{273+100}{273+0}) = \underline{23.52 \text{ J/K}}$$

c) 18-gram of water at 100 °C is changed to steam at 100 °C . [$L_v = 22.6\times10^5$ J/kg]

✓ $$dS_3 = \frac{dQ_r}{T} = \frac{mL_v}{T} = \frac{0.018\times(22.6\times10^5)}{273+0} = \underline{109.1 \text{ J/K}}$$

d) 18-gram ice cube at 0 °C is changed to steam at 100 °C.

✓ $$dS = dS_1 + dS_2 + dS_3 = \underline{154.6 \text{ J/K}}$$

➔ Two moles of an ideal monatomic gas undergo a reversible isothermal expansion from 0.1 m³ to 0.5 m³ at a temperature of 20 °C. What is the change in entropy of the gas?

✓ $$\Delta S = nR\int_i^f \frac{dV}{V} = nR\ln(\frac{V_f}{V_i}) = 2\times8.314\times\ln(\frac{0.5}{0.1}) = \underline{26.7 \text{ J/K}}$$

➔ One mole of an ideal monatomic gas is heated quasi-statically at constant volume from 100 K to 105 K. What is the change in entropy of the gas?

✓ $$\Delta S = nC_v\int_i^f \frac{dT}{T} = nC_v \ln(\frac{T_f}{T}) = 1\times\frac{3}{2}\times8.314\times\ln(\frac{105}{100}) \approx \underline{0.61 \text{ J/K}}$$

✓ Or one can use the following approximate method,

$$\Delta S = \frac{dQ}{T} = nRC_v \frac{105\text{-}100}{102.5} = 1(\frac{3}{2}\times 8.314)\frac{5}{102.5} \approx \underline{0.61\text{ J/K}}$$

➔ If 200 g of water at 20 ^{o}C is mixed with 300 g of water at 75 ^{o}C, find:

a- the final equilibrium temperature of the mixture and

✓ First, calculate the heat lost by 300 g and the heat gained by the 200 g,

$$Q\,(\text{lost by 300 g}) = Q_1 = 300C_{water}\left(T_f - 75\right)$$

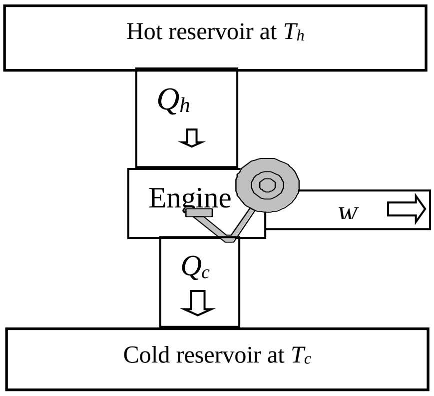
$$Q\,(\text{gained by 200 g}) = Q_2 = 200C_{water}\left(T_f - 20\right)$$

Use the fact that $Q_1 + Q_2 = 0$, one can solve and find $T_f = 53.0\ ^o\text{C}$.

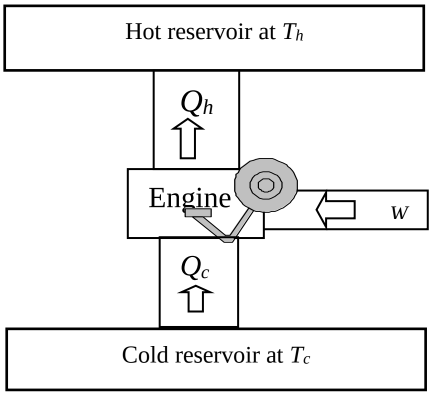
b- the change in entropy of the system.

$$\begin{aligned}\Delta\text{S} &= 300C_{water}\ln(\frac{53+273}{75+273}) + 300C_{water}\ln(\frac{53+273}{20+273})\\ &= (-82.010 + 89.35)\ \frac{\text{J}}{\text{K}} = 7.34\ \frac{\text{J}}{\text{K}}\end{aligned}$$

Heat engine: any device that works in a cycle, extracting (or absorbing or takes in) heat, Q_h, from a hot reservoir doing work (*W*), and exhausting (or rejected or expelled) remaining heat, Q_c, into a cold reservoir. Q_c makes the pollutions of our environment.



Heat engine



Refrigerator

The efficiency (e) of the heat engine is given by:

$$e = \frac{\text{Energy we get}}{\text{Energy we pay for}} = \frac{W}{Q_h} = \frac{|Q_h| - |Q_c|}{|Q_h|}$$

The power is

$$P\ [\text{Watt}] = \frac{W\ [\text{Joule}]}{t\ [\text{Seconds}]} \quad \Rightarrow \quad e = \frac{W/t}{Q_h/t} = \frac{P}{Q_h/t}$$

➔ An automobile engine operates with an overall efficiency of 20%. How many gallons of gasoline are wasted for each 10 gallons burned?

✓
$$e = \frac{W}{Q_h} = \frac{|Q_h| - |Q_c|}{|Q_h|}$$

$$\Rightarrow 0.2 = \frac{10 - |Q_c|}{10} \quad \Rightarrow \quad |Q_c| = \underline{8 \text{ gallons}}$$

➔ An engine absorbs 1600 J from a hot reservoir and expels 1000 J to a cold reservoir in each cycle.

a. What is the efficiency, e, of the engine?

✓
$$e = \frac{W}{Q_h} = \frac{|Q_h| - |Q_c|}{|Q_h|} = \frac{1600 - 1000}{1600} = \underline{0.375} \text{ or } \underline{37.5\%}$$

b. How much work is done, W, in each cycle?

✓ $W = Q_h - Q_c = 1600 - 1000 = \underline{600 \text{ J}}.$

c. What is the power output of the engine if each cycle lasts for 0.3 s?

✓
$$P = \frac{W}{t} = \frac{600 \text{ J}}{0.3 \text{ s}} = \underline{2000 \text{ Watt}}.$$

Carnot cycle: is the most efficient cycle possible for a heat engine. An engine that operates in accordance to this cycle between a hot reservoir, T_h, and a cold reservoir, T_h, has the ratio $\frac{|Q_h|}{|Q_c|} = \frac{T_h}{T_c}$ and the maximum efficiency

$$e = \frac{T_h - T_c}{T_h}$$

NOTE THAT: **Kelvin Temperature must be used in the above equations**.

➔ A Carnot engine has a power output, *P*, of 200 W and operates between two reservoirs at $27\ ^{o}\text{C}$ and $327\ ^{o}\text{C}$.

a- Find the maximum efficiency of the engine

✓
$$e = \frac{T_h - T_c}{T_h} = \frac{(273+327)-(273+27)}{(273+327)} = \frac{300}{600} = 0.5$$

b- How much energy is absorbed per hour?

✓ Use the efficiency in the form:

$$e = \frac{W/t}{Q_h/t} = \frac{P}{Q_h/t} \qquad \Rightarrow \quad \frac{Q_h}{t} = \frac{P}{e} = \frac{200}{0.5} = 400 \text{ Watt}.$$

For one hour,

$$Q_h = (4.0\times10^2 \text{ J/s})(3600 \text{ s}) = 1.44\times10^6 \text{ J}.$$

c- How much heat energy is rejected per hour?

✓ You can use:
$$Q_c = Q_h - W = Q_h - Pt$$
$$= 1.44\times10^6 \text{ J} - (2\times10^2 \text{ W})(3600 \text{ s}) = 7.2\times10^5 \text{ J}.$$

Or you can use:
$$Q_c = Q_h (\frac{T_h}{T_c})$$
$$= 1.44\times10^6 (\frac{300}{600}) = 7.2\times10^5 \text{ J}$$

➔ A heat engine operating between 200 °C and 80 °C achieves 20% of the maximum possible efficiency.

a. What is the maximum possible efficiency?

✓ $$e_{\max} = e_{\text{Carnot}} = \frac{T_h - T_c}{T_h} = \frac{353 - 473}{353} = 0.254$$

b. What is the actual efficiency?

✓ $$e_{actual} = 0.2\times e_{\max} = 0.2\times 0.254 = 0.051$$

c. What energy input will enable the engine to perform 10^4 J of work?

$\Rightarrow$ $$e_{\text{actual}} = \frac{W}{Q_h} \quad \Rightarrow \quad Q_h = \frac{W}{e_{\text{actual}}} = \frac{10^4}{0.051} = 1.97\times10^5 \text{ J}.$$

Heat pumps and Refrigerator: A heat pump, or refrigerator, is a device that moves heat from a reservoir at a low temperature, Q_c, to one at higher temperature, Q_h. Mechanical work, *W*, must be supplied to the heat pump in order to accomplish this.

The coefficient of performance (COP) of a **refrigerator** is defined by:

$$COP = \frac{\text{what we want}}{\text{what we pay for}} = \frac{|Q_c|}{W} = \frac{|Q_c|}{|Q_h| - |Q_c|} = \frac{T_c}{T_h - T_c}$$

The coefficient of performance (COP) of a **heat pump** is defined by:

$$COP(\text{heat pump}) = \frac{1}{e} = \frac{|Q_h|}{W} = \frac{|Q_h|}{|Q_h| - |Q_c|} = \frac{T_h}{T_h - T_c}$$

➔ What is the coefficient of performance of a heat pump that brings heat from the outdoors at - 3.0 °C into + 22 °C house? (Hint: the heat pump does work, *W*, which is also available to heat the house.)

✓ $$COP(\text{heat pump}) = \frac{T_h}{T_h - T_c}$$
$$= \frac{(273+22)}{(273+22)-(273-3)} = \frac{295}{25} = 11.8$$

True-False Questions

1- Liquid water has less entropy than ice. T
2- The entropy of a system can never decrease. F
3- Crystals are less disordered than gases. T
4- The most efficient cyclic process is the Carnot cycle. T
5- A refrigerator (heat pump) is a heat engine working in reverse. T
6- It is impossible to construct a heat engine which does work without rejecting some heat to a cold reservoir. T
7- Entropy is a quantity used to measure the degree of disorder in a system. T
8- The total entropy decreases for any system that undergoes an irreversible process. F
9- The total entropy of a system increases only if it absorbs heat. F
10- No heat engine has higher efficiency than Carnot efficiency. T
11- The efficiency of the ideal engine should be greater than one. F
12- No change in entropy for a system goes in reversible cyclic process. T
13- If the steam is condensed, its entropy will decrease. T
14- The coefficient of performance of refrigerator should be less than one. F
15- Isolated systems tend toward disorder and entropy is a measure of this disorder. T
16- The entropy of the universe decreases in any process. F
17- The efficiency of heat engines can be 100%. F
18- Heat engines can have efficiency higher than Carnot engine working between the same two temperatures. F
19- To calculate the efficiency of ideal engine the temperature should be in Celsius. F
20- The thermal efficiency of an ideal engine can be = 1.0. F
21- For any process the change in entropy of a closed system < 0. F

Kinetic theory of gases: is a sub-branch of statistical mechanics in which no attempt is made to derive the thermodynamic laws, but rather their meaning in terms of averages of microscopic variables is made clearer. Basic assumptions:

1- the system (gas) consists of identical particles, of negligible volume (compared with the volume of the gas), called molecules.
2- the molecules are perfectly elastic, i.e. no energy lost in collision,
3- the time of collision is negligible compared with the time between collisions,
4- the attraction between the molecules is negligible. In these conditions, the gas is ideal. The molecules in the gas obey Newton's law and move randomly with a wide distribution of speeds ranging from zero to very large values.

Equipartition of energy theorem: states that "*The average kinetic energy per molecule per degree of freedom is (1/2) kT*". Consequently, the average translational kinetic energy per molecule is given by

$$\overline{K} = \frac{1}{2} m \overline{v^2} = \frac{3}{2} kT.$$

where T is the absolute temperature. The pressure is

$$P = \frac{NkT}{V} = \frac{2}{3}\frac{N}{V}\overline{K}.$$

➔ 5-liter vessel contains nitrogen at a temperature of 27 °C and a pressure of 3 atm. Find

a. the average kinetic energy per molecules.

✓ $$\overline{K} = \frac{1}{2} m \overline{v^2} = \frac{3}{2} kT = \frac{3}{2}\frac{RT}{N_A} = \frac{3}{2}\frac{(8.314)(300)}{6.02\times10^{23}} = \underline{6.21\times10^{21}\ \text{J}}.$$

b. the total translational kinetic energy of the gas,

✓ $$K_{total} = N\,\overline{K} = \frac{3}{2} PV = \frac{3}{2}(3\times1.01\times10^{5})\times(5\times10^{-3}) = \underline{2.27\times10^{3}\ \text{J}}.$$

c. the total number, N, of nitrogen atoms and the number of moles, n.

✓ $$N = \frac{K_{total}}{\overline{K}} = 3.66\times10^{23} \text{ atoms.}$$

✓ $$n = \frac{N}{N_A} = \frac{3.66\times10^{23}}{6.02\times10^{23}} = 0.61 \text{ mole.}$$

➔ A cylinder contains a mixture of helium and argon gas in equilibrium at a temperature of 150 °C. What is the average kinetic energy of each gas molecule?

For helium:

✓ $$\overline{K} = \frac{3}{2}\, kT = \frac{3}{2}(1.38\times10^{-23}\ \frac{\text{J}}{\text{K}})(423\text{K}) = 8.76\times10^{-21}\ \text{J}.$$

For Argon, Since the average kinetic energy depends only on the absolute temperature, so the average kinetic energy for argon will be the same as for helium, i.e. 8.76×10^{-21} J.

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where T is the absolute temperature. The pressure is

$$P = \frac{NkT}{V} = \frac{2}{3}\frac{N}{V}\overline{K}.$$

Proof: Due to the collision between the incident particle and the wall,

$$\text{Change of momentum of the incident particle } = \Delta p_x = (-m\,\mathrm{v}_x) - (m\,\mathrm{v}_x) = -2m\,\mathrm{v}_x$$

$$\text{The momentum delivered to the wall } = 2m\,\mathrm{v}_x$$

From Newton's second law, the force acting on the wall will be:

$$F_x = \frac{\Delta p_x}{\Delta t} = \frac{2m\,\mathrm{v}_x}{2L/\mathrm{v}_x} = \frac{m\,\mathrm{v}_x^2}{L}$$

And the pressure "P" will be:

$$\mathrm{P} = \frac{F_x}{L^2} = \frac{\dfrac{m\,\mathrm{v}_{x1}^2}{L} + \dfrac{m\,\mathrm{v}_{x2}^2}{L} + \cdots + \dfrac{m\,\mathrm{v}_{xN}^2}{L}}{L^2}$$

$$= \frac{m}{L^3}\left(\mathrm{v}_{x1}^2 + \mathrm{v}_{x2}^2 + \cdots + \mathrm{v}_{xN}^2\right)$$

$$= \frac{m}{L^3}\left(N = nN_A\right)\frac{\left(\mathrm{v}_{x1}^2 + \mathrm{v}_{x2}^2 + \cdots + \mathrm{v}_{xN}^2\right)}{N}$$

$$= \frac{nmN_A}{L^3}\left(\mathrm{v}_x^2\right)_{average} = \frac{nM}{V}\overline{\mathrm{v}_x^2}$$

In three dimension, we have $\overline{\mathrm{v}_x^2} = \frac{1}{3}\overline{\mathrm{v}^2}$, then:

$$\mathrm{P} = \frac{nM}{3V}\overline{\mathrm{v}^2}$$

Define $\mathrm{v}_{\mathrm{rms}}^2 = \sqrt{\overline{\mathrm{v}^2}}$, then:

$$\boxed{\mathrm{P} = \frac{nM}{3V}\mathrm{v}_{\mathrm{rms}}^2}$$

But, from the ideal gas law $\mathrm{P}V = nRT$, one can find:

$$\boxed{\mathrm{v}_{\mathrm{rms}} = \sqrt{\frac{3RT}{M}}}$$

The average translational kinetic energy:

$$\mathrm{K}_{\mathrm{ave}} = \left(\frac{1}{2} m\, \mathrm{v}^2\right)_{ave} = \frac{1}{2} m\, \overline{\mathrm{v}^2} = \frac{1}{2} m\, \mathrm{v}_{\mathrm{rms}}^2 = \frac{1}{2} m \left(\frac{3RT}{M}\right) = \frac{1}{2}\left(\frac{3RT}{N_A}\right) = \frac{3}{2} kT$$

$$E_{\mathrm{int}} = N\mathrm{K}_{\mathrm{ave}} = \frac{3}{2} NkT = \frac{3}{2} nRT$$

Case 1: At constant volume:

$W = p\Delta V = 0,$

$Q = nC_V\, \Delta T$, $C_V \equiv$ molar specific heat at constant volume.

$\Delta \mathrm{E}_{\mathrm{int}} = Q = nC_V\, \Delta T$, for ideal gas and for any process.

Compare with the expression:

$$\Delta E_{\mathrm{int}} = \frac{3}{2} nR\, \Delta T$$

This implies that: $C_V = \frac{3}{2} R = 12.5\ \frac{\mathrm{J}}{\text{mole K}}$

Case 1: At constant pressure:

$W = pV \quad \Rightarrow \quad \Delta W = p\Delta V = nR\,\Delta T$,

$Q = nC_P \Delta T$, $C_V \equiv$ molar specific heat at constant pressure.

$\Delta Q = \Delta \mathrm{E}_{\mathrm{int}} + p\Delta V$,

$$nC_P \Delta T = nC_V\, \Delta T + nR\,\Delta T \quad \Rightarrow \quad \boxed{C_P = C_V + R}$$