General Physics II at EPFL

(2018-2019 SS, Wed 17:15-19:00 and Thu 8:15-10:00, Exercise Thu 10:15-12:00)

Thermodynamic (5th week)

Thermodynamical State

A thermodynamic state is described by a set of state variables. Examples of state variables are, P, V, T, number of moles, E_{int} etc. They are uniquely defined, independent of how the system arrived at that particular state. As seen later, heat or work are not state variables since they depend on how the system reached the particular state. Once a sufficient numbers of variables have bees specified, all other variables are uniquely determined. The number of variables needed to specify the system depends on the system.

Example: System of an ideal gas

The gas law for ideal gas $PV = NkT$ shows that a set of three variables out of four, i.e. P, V, T, and N determines the system.

The First Low of Thermodynamics

Extending the concept of the energy conservation to the thermodynamical system. In a closed system, we have

$$\Delta E_{\text{int}} = Q - W$$

ΔE_{int}; Change of the internal energy, Q: heat into the system, W: work by the system
In the isolated system, no energy transfer can occur, i.e. $Q = 0$ and $W = 0$, hence $\Delta E_{\text{int}} = 0$.

Thermal Processes

There are the following four thermal processes for gas to change its state:

Isothermal ($\Delta T = 0$): while the state changes, the temperature is kept constant.
Adiabatic ($Q = 0$): process with no heat, i.e. thermally isolated system or a very fast process.
Isobaric ($\Delta P = 0$): while the state changes, the pressure is kept constant.
Isovolumetric ($\Delta V = 0$): while the state changes, the volume is kept constant.

Molecular Specific Heat

Recall the specific heat, c, for solid and liquid:

$$Q = mc\Delta T$$

where the heat Q is in cal, m is the mass in g and ΔT the temperature difference in degree Celsius. For the gas, two more variables, volume (V) and pressure (P), are needed in consideration. Therefore, two kinds of specific heats are introduced:

c_{V}: specific heat at constant volume
c_{P}: specific heat at a constant pressure.
and they are fairly different.

	Specific heats cal / (g K)		molar specific heats cal / (mol K)			
	c_V	c_P	C_V	C_P	$C_\mathrm{P} - C_\mathrm{V}$	$\gamma = C_\mathrm{P}/C_\mathrm{V}$
Monatomic						
He	0.75	1.15	2.98	4.97	1.99	1.67
Ne	0.15	0.25	2.98	4.97	1.99	1.67
Diatomic						
N_2	0.177	0.248	4.96	6.95	1.99	1.40
O_2	0.155	0.218	5.03	7.03	2.00	1.40
Triatomic						
CO_2	0.153	0.199	6.80	8.83	2.03	1.30
H_2O (100°C)	0.350	0.482	6.20	8.20	2.00	1.32

Similarly, we can have those specific heats for N_A gas molecules, where

$$N_\mathrm{A} = 6.02 \times 10^{23}$$

N_A is the Avogadro number, called molar Specific Heats, C_V and C_P. The heat needed to raise the temperature of n moles of gas, i.e. with $n \times N_\mathrm{A}$ molecules, by ΔT in C° is given by

$$Q_\mathrm{V} = nC_\mathrm{V}\Delta T \quad \text{volume constant}$$

$$Q_\mathrm{P} = nC_\mathrm{P}\Delta T \quad \text{pressure constant}$$

For a gas with r u molecular mass, mass of the 1 mole of the gas is r g. Therefore,

$$C_\mathrm{V} = r \cdot c_\mathrm{V}$$

$$C_\mathrm{P} = r \cdot c_\mathrm{p}$$

By noting that the atomic mass of the He, Ne, N_2 etc. are given by, ~4 u, ~20 u, ~28 u, etc., respectively, the table shows that indeed this relation is valid. The gas is heated very slowly under

1) a constant volume V, or

2) a constant pressure P,

to change the temperature from T to $T+\Delta T$.

For 1), $\Delta V=0$, i.e. no work is done, i.e. from $\Delta E_\mathrm{int} = Q - W$

$$\Delta E_\mathrm{int} = Q_\mathrm{V} = nC_V\Delta T$$

all the thermal energy into the system is used to change the internal energy. For an infinitesimally small changes, we have

$$C_\mathrm{V} = \frac{1}{n}\left(\frac{\Delta E_\mathrm{int}}{\Delta T}\right)_{V=\mathrm{constant}} \equiv \frac{1}{n}\left(\frac{\partial E_\mathrm{int}}{\partial T}\right)_V .$$

The process 2) requires

$$\Delta E_\mathrm{int} = Q_\mathrm{P} - W$$

where the work $W = P\Delta V$, since $\Delta V \neq 0$ and P is constant. Noting that ΔE_int are identical for the two processes given the same change in the temperature, ΔT, it follows that $Q_\mathrm{V} = Q_\mathrm{P} - W$, i.e.

$$Q_\mathrm{P} - Q_\mathrm{V} = W = P\Delta V$$

where the work is in the isobaric process, i.e. P is constant. For an ideal gas, $PV = nRT$, with a constant pressure we obtain

$$\Delta V = \frac{nR\Delta T}{P}$$

leading to

$$Q_\mathrm{P} - Q_\mathrm{V} = P\frac{nR\Delta T}{P} = nR\Delta T$$

Combined with $Q_\mathrm{P} = nC_\mathrm{P}\Delta T$ and $Q_\mathrm{V} = nC_\mathrm{V}\Delta T$, it follows that

$$C_\mathrm{P} - C_\mathrm{V} = R$$

i.e. $C_\mathrm{P} > C_\mathrm{V}$, i.e. more heat is needed for the constant pressure to raise the temperature to compensate the work done at the same time. Note that the gas constant is given by

$$R = 8.314\frac{\mathrm{J}}{\mathrm{mol\cdot K}} = 1.99\frac{\mathrm{cal}}{\mathrm{mol\cdot K}}$$

which is close to the values given experimentally for various gasses.

Equipartition of Energy

In the kinetic theory of the point like ideal gas discussed previously, we obtained

$$PV = Nm\langle v_x^2\rangle = \frac{2}{3}N\left(\frac{m}{2}\langle v^2\rangle\right) = \frac{2}{3}N\langle K\rangle$$

where $\langle K\rangle$ is the average translational kinetic energy and $N\langle K\rangle$ is equivalent to the internal energy of the gas. Together with the ideal gas law, $PV = nRT$, it follows that

$$E_\mathrm{int} = \frac{3nRT}{2}$$

In the process with a constant volume, $W = 0$ and

$$\Delta E_\mathrm{int} = Q_\mathrm{V} = nC_\mathrm{V}\Delta T$$

thus

$$C_\mathrm{V} = \frac{1}{n}\left(\frac{\Delta E_\mathrm{int}}{\Delta \mathrm{T}}\right) = \frac{3}{2}R$$

From the value of R, we obtain $C_\mathrm{V} = 2.98\,\mathrm{cal/mol\cdot K}$, in a good agreement with monatomic gasses. We now recall the Boltzmann factor $e^{-E/kT}$ describing the distribution of the internal energy E for a temperature T. Let us assume that the energy has a function of variable x as form $E = \alpha x^2$ with a constant α. The average energy $\langle E\rangle$ is then given by

$$\langle E\rangle = \frac{\int_{-\infty}^{\infty}\alpha x^2 e^{-\alpha x^2/kT}dx}{\int_{-\infty}^{\infty}e^{-\alpha x^2/kT}dx} = \frac{kT}{2}$$

If we extend the energy to be

$$E = \sum_{i=1}^{n_f}\alpha_i x_i^2$$

i.e. the energy is a sum of n_f components, all having a same functional form. The average energy is then becomes,

$$\langle E\rangle = \frac{\int_{-\infty}^{\infty}dx_1\cdots\int_{-\infty}^{\infty}dx_{n_f}\sum_{i=1}^{n_f}\alpha_i x_i^2 e^{-\sum_j\alpha_j x_j^2/kT}}{\int_{-\infty}^{\infty}dx_1\cdots\int_{-\infty}^{\infty}dx_{n_f}e^{-\sum_j\alpha_j x_j^2/kT}} = \sum_{i=1}^{n_f}\frac{\int_{-\infty}^{\infty}dx_1\cdots\int_{-\infty}^{\infty}dx_{n_f}\alpha_i x_i^2 e^{-\sum_j\alpha_j x_j^2/kT}}{\int_{-\infty}^{\infty}dx_1\cdots\int_{-\infty}^{\infty}dx_{n_f}e^{-\sum_j\alpha_j x_j^2/kT}}$$

Since all the but one integrals cancel between the numerators and denominators, we have

$$\langle E\rangle = \sum_{i=1}^{n_f}\frac{\int_{-\infty}^{\infty}dx_i\alpha_i x_i^2 e^{-\alpha_i x_i^2/kT}}{\int_{-\infty}^{\infty}dx_i e^{-\alpha_i x_i^2/kT}} = \frac{n_f}{2}kT$$

For a gas of N molecules, or n mole, it follows that

$$\langle E\rangle = \frac{n_f}{2}NkT \text{ or } \langle E\rangle = \frac{n_f}{2}nRT$$

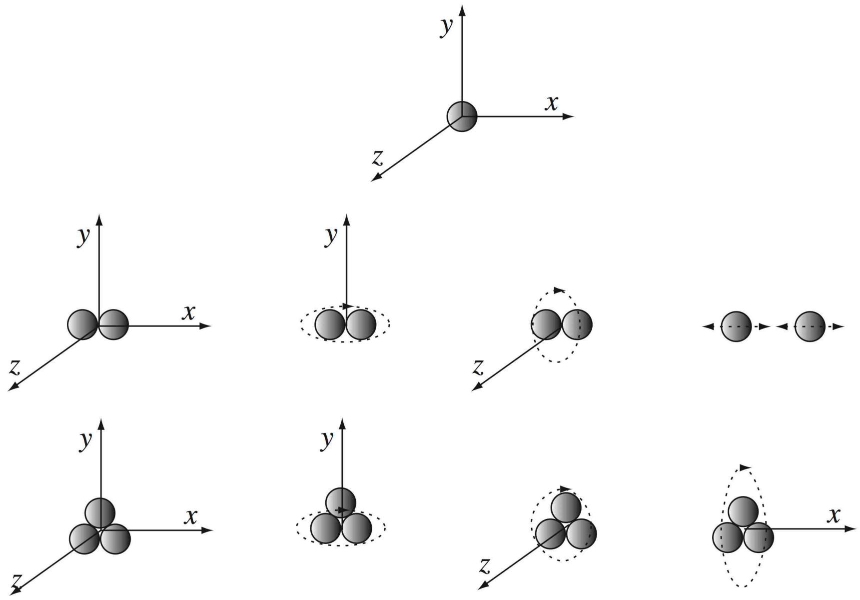
respectively. It follows that

$$C_\text{V} = \frac{1}{n}\left(\frac{\Delta E_\text{int}}{\Delta \text{T}}\right) = \frac{n_f}{2}R$$

A mono atomic gas has only translational degrees of freedom and the energy is given by

$$E = \frac{m}{2}\left(v_x^2 + v_y^2 + v_z^2\right)$$

i.e. $n_f = 3$. More complex molecules have rotational kinetic energies, in addition to the translational kinetic energies.



For example, diatomic molecules have two and triatomic molecules three degrees of freedom and the kinetic energy is given by

$$E = \frac{m}{2}\left(v_x^2 + v_y^2 + v_z^2\right) + \frac{L_1^2}{2I_1} + \frac{L_2^2}{2I_2} \text{ and } E = \frac{m}{2}\left(v_x^2 + v_y^2 + v_z^2\right) + \frac{L_1^2}{2I_1} + \frac{L_2^2}{2I_2} + \frac{L_3^2}{2I_3}$$

respectively, where L's are the angular momenta and I's corresponding moments, i.e. $n_f = 5$ and 6. Energy of diatomic gas with vibration is given by

$$E = \frac{m}{2}\left(v_x^2 + v_y^2 + v_z^2\right) + \frac{L_1^2}{2I_1} + \frac{L_2^2}{2I_2} + \frac{\mu}{2}\left(\dot{\vec{r}}_1 - \dot{\vec{r}}_2\right)^2 + \frac{k}{2}\left(\vec{r}_1 - \vec{r}_2\right)^2$$

where μ is the reduced mass of the two atoms and k is the spring constant, i.e. $n_f = 7$.

Here are some considerations:

Monatomic molecule: 3-translational kinetic energies, $n_f = 3$

Diatomic molecule: plus 2-rotational kinetic energies, $n_f = 5$

Diatomic molecule: plus1-vibrational kinetic and 1-vibrational potential energies, $n_f = 7$

It seems that energy of a molecule is equally shared among the active degrees of freedom and the each degree of freedom caries in average $kT/2$ of the energy. This is called equipartition theorem.

Note that

$$\frac{3}{2}R = 2.98\,\text{cal/mol}\cdot\text{K},\ \frac{5}{2}R = 4.98\,\text{cal/mol}\cdot\text{K},\ \frac{7}{2}R = 6.97\,\text{cal/mol}\cdot\text{K}$$

Measured values show that 1) some of the degrees of freedom are not "active", and 2) decreases with temperature to $n_\mathrm{f} = 5$ then to $n_\mathrm{f} = 3$ for different gas molecules, i.e. gasses behave like a monatomic molecule at a very low temperature. These observations are related to the foundation of quantum theory.

Change of internal energy for ideal gas

For isovolumetric process, we have $\Delta V = 0$, thus

$$\Delta E_\mathrm{int} = Q_\mathrm{V} = nC_\mathrm{V}\Delta T$$

and for isobaric process

$$\Delta E_\mathrm{int} = nC_\mathrm{P}\Delta T - P\Delta V$$

For ideal gas, we have $C_\mathrm{P} - C_\mathrm{V} = R$ and $\Delta V = nR\Delta T/P$, thus

$$\Delta E_\mathrm{int} = n\left(C_\mathrm{V} + R\right)\Delta T - nR\Delta T = nC_\mathrm{V}\Delta T$$

i.e. the change of internal energy for a temperature change of ΔT is given by

$$\Delta E_\mathrm{int} = nC_\mathrm{V}\Delta T$$

for both isovolumetric and isobaric processes. For ideal gas, any change in two thermal states can be made as combinations of Isovolumetric and isobaric processes, the change of internal energy for a temperature change of ΔT **for any processes is given by**

$$\Delta E_\mathrm{int} = nC_\mathrm{V}\Delta T \ .$$

Adiabatic Process

As mentioned, for a defined gas, among three state variables, T, V and P, there are only two independent variables. Let us use T and V, leading to

$$\Delta E_\mathrm{int} = \left(\frac{\partial E_\mathrm{int}}{\partial V}\right)_T \Delta V + \left(\frac{\partial E_\mathrm{int}}{\partial T}\right)_V \Delta T \ .$$

for a very small change of the state, i.e. $|\Delta V/V| \ll 1$ and $|\Delta P/P| \ll 1$, and also

$$W = \int_{V_\mathrm{i}}^{V_\mathrm{i}+\Delta V} P(V)dV \approx P(V_\mathrm{i}) \int_{V}^{V+\Delta V} dV = P\Delta V$$

The first law of thermodynamics gives

$$\Delta E_\mathrm{int} = Q - W = Q - P\Delta V \ .$$

By combining the two equations, we obtain

$$Q = P\Delta V + \left(\frac{\partial E_\mathrm{int}}{\partial V}\right)_T \Delta V + \left(\frac{\partial E_\mathrm{int}}{\partial T}\right)_V \Delta T \ .$$

For ideal gas, recalling that the internal energy depends only on the temperature, i.e. $\left(\partial E_\mathrm{int}/\partial V\right)_T = 0$ and the definition of C_V, it follows that

$$Q = P\Delta V + nC_V\Delta T \ .$$

In an adiabatic process, no heat is allowed. This can happen when the system is thermally well isolated or the process happens very fast. Let us consider a very slow (quasistatic) process where the state of ideal gas is adiabatically changed from A:$\left(V_\mathrm{a}, P_\mathrm{a}, T_0\right)$ to C:$\left(V_\mathrm{b}, P_\mathrm{c}, T_\mathrm{c}\right)$, i.e. C has the same volume as B. Since there is no heat involved in the process, $Q = 0$, thus

$$P\Delta V + nC_V\Delta T = 0 \ .$$

Using $PV = nRT$ for the ideal gas, we obtain

$$\frac{\Delta V}{V}+\frac{C_V}{R}\frac{\Delta T}{T}=0$$

and further more,

$$\Delta T=\frac{P\Delta V+V\Delta P}{nR} \text{ and } T=\frac{PV}{nR}$$

lead to

$$\frac{\Delta V}{V}+\frac{C_V}{R}\left(\frac{\Delta V}{V}+\frac{\Delta P}{P}\right)=0 .$$

It follows that

$$\left(R+C_V\right)\frac{\Delta V}{V}+C_V\frac{\Delta P}{P}=C_P\frac{\Delta V}{V}+C_V\frac{\Delta P}{P}=0$$

i.e.

$$\gamma\frac{\Delta V}{V}+\frac{\Delta P}{P}=0$$

where, $\gamma=C_{\mathrm{P}}/C_{\mathrm{V}}>1$. By replacing ΔV and ΔP by $\mathrm{d}V$ and $\mathrm{d}P$, respectively, integration gives

$$\gamma\ln V+\ln P=\ln V^{\gamma}+\ln\mathrm{P}=\ln\left(V^{\gamma}\mathrm{P}\right)=\text{constant}$$

leading to

$$V^{\gamma}P=\text{ constant} .$$

Special demonstration

Let us consider two states A:$\left(V_{\mathrm{a}},\, P_{\mathrm{a}},\, T_0\right)$ to B:$\left(V_{\mathrm{b}},\, P_{\mathrm{b}},\, T_0\right)$ of the same gas, where $V_{\mathrm{a}}<V_{\mathrm{b}}$. Since the temperatures are the same, the internal energy at A and B are the same, i.e.

$$\Delta E_{\mathrm{int}}=E_{\mathrm{int:b}}-E_{\mathrm{int:a}}=0$$

From the first law of thermodynamic

$$\Delta E_{\mathrm{int}}=Q-W$$

it follows that

$$Q=W_{\mathrm{a}\to\mathrm{b}}$$

i.e. if work is done, there must be heat.

We now determine the work for two different paths.

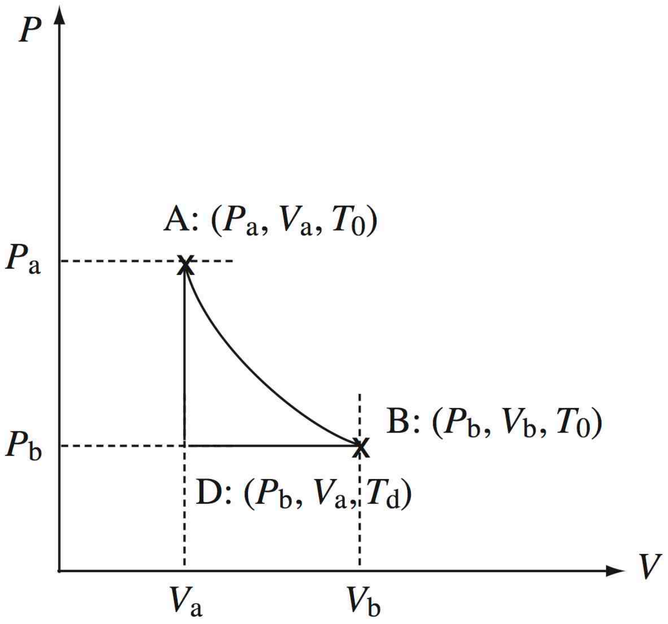
1) Work done for the isothermal expansion of an ideal gas from A to B at the temperature T_0. From the ideal gas law,

$$P=\frac{nRT_0}{V}$$

the work is given by

$$W_{1:\mathrm{a}\to\mathrm{b}}=\int_{V_{\mathrm{a}}}^{V_{\mathrm{b}}}P\,dV=\int_{V_{\mathrm{a}}}^{V_{\mathrm{b}}}\frac{nRT_0}{V}dV=nRT_0\int_{V_{\mathrm{a}}}^{V_{\mathrm{b}}}\frac{dV}{V}=nRT_0\ln V\Big]_{V_{\mathrm{a}}}^{V_{\mathrm{b}}}=nRT_0\ln\frac{V_{\mathrm{b}}}{V_{\mathrm{a}}}>0$$

Note that from the ideal gas law, $P_{\mathrm{a}}>P_{\mathrm{b}}$ and W corresponds to the area under the $P(V)$ line.



2) Work done for the isovolumeric process from $P = P_a$ to $P = P_b$, with constant $V = V_a$ to the state D: (V_a, P_b), followed by the isobaric process with a constant $P = P_b$ from $V = V_a$ to $V = V_b$.
For the isovolumeric part,

$$W_{a \to d} = \int_{V_a}^{V_a} P\,dV = 0$$

i.e. no work is done. Note that at D: (V_a, P_b), the temperature has to change. This can be seen by comparing the equation of the state at a, and d,

$$T_0 = \frac{P_a V_a}{nR}, \; T_d = \frac{P_b V_a}{nR}$$

and

$$T_d - T_0 = \frac{V_a}{nR}(P_b - P_a) < 0$$

i.e. the temperature drops. In the second process, $P = P_b$ and the work is given by

$$W_{d \to b} = \int_{V_a}^{V_b} P_b\,dV = P_b \int_{V_a}^{V_b} dV = P_b V \Big]_{V_a}^{V_b} = P_b (V_b - V_a) > 0$$

In this process, the temperature has to increases from T_d to T_0. The total work done is

$$W_{2:a \to b} = W_{a \to d} + W_{b \to b} = P_b (V_b - V_a)$$

With the ideal gas law,

$$P_b = \frac{nRT_0}{V_b}$$

it follows that

$$W_{2:a \to b} = P_b (V_b - V_a) = nRT_0 \left(1 - \frac{V_a}{V_b}\right)$$

Note that

$$W_{1:a \to b} \neq W_{2:a \to b}$$

i.e. the work done depends on the path of the process. In both cases, the work is positive hence there must be the heat into the gas. Since $Q = W$, the heat Q also depends on the process.