Thermodynamics Lecture Notes: Chapter 6

Michaela Hirschmann

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6 Energy, Heat, and Work

6.1 Energy and heat in thermodynamics

Energy

A unit of energy, related to thermal energy:
1 calorie (cal) = energy needed to increase the temperature of 1 g of water by 1 Celsius degree
1 cal = 4.186 J = 4.186 Nm

Temperature T in Kelvin: a measure of the average kinetic energy of individual molecules.

Internal Energy E_{int}: total energy contained by a thermodynamic system

$$E_{int} = \text{thermal energy} + \text{potential energy} \tag{1}$$

Thermal energy is kinetic energy due to translation, rotation and vibration, directly linked to the temperature.

Internal energy of an *ideal* gas: no potential energy, i.e. internal energy is equal to the thermal energy. Thermal energy is only due to translational kinetic energy of all the gas molecules.

$$E_{int} = E_{kin} = N\frac{m\langle v^2\rangle}{2} = \frac{3}{2}NkT = \frac{3}{2}nRT \tag{2}$$

where N is the number of molecules and n number of moles of the gas.

Flow of energy: Heat and work

Work (W): flow of energy out from the system in mechanics not related to temperature.
Heat (Q): flow of energy into the system due to the difference in temperature.
They can be transferred from one system to another. They do not define the state of a system, i.e. they are not state variables.

Open, Closed and Isolated System

Closed system: can exchange energy but not matter with the surroundings.
Isolated system: can exchange neither energy nor matter with the surroundings.
Open system: can exchange both energy and matter with surroundings.

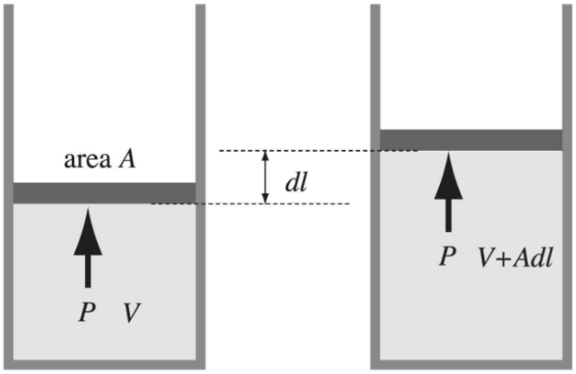
Work

When the volume of a thermodynamic system changes, work is done. Consider a cylindrical container with a movable piston, which is filled with gas, not experiencing friction with the wall. If we change the volume in a quasi-statical way, at any instance of the state change, the gas is in an equilibrium state, i.e. T and P are uniform in the gas. The gas pressure pushes the piston generating a force, $F = PA$ where A is the area of the piston. The work, done to move the piston by an infinitesimal amount dl, is given by

$$dW = Fdl = PAdl = PdV \tag{3}$$

where $dV = Adl$ is the infinitesimal change of the volume. Note that when the piston is pushed up, work is done by the gas. When the volume changes from V_a to V_b, the work done is given by

$$W = \int_{V_a}^{V_b} PdV \tag{4}$$



6.2 Heat capacity and calorimetry

We distinguish between sensible and latent heat. The latter is described in section 6.4, while here we focus on sensible heat. For sensible heat, heat going into the system, Q, changes the temperature of the system by ΔT:

$$Q = mc\Delta T \tag{5}$$

where m is the mass of the material in the system and c is a quantity characteristic to the material called "specific heat". The unit of c is given by $\frac{J}{kg.C^\circ}$ or $\frac{kcal}{kg.C^\circ}$. From the definition of the calorie, c for the water at $15°C$ and a constant pressure of 1 atm is $1\frac{kcal}{kg\ °C^\circ}$.

Example:
We consider a system of an iron container of 20 kg, containing 20 kg of water. The specific heat for iron is $0.11\frac{kcal}{kg.C^\circ}$. Now we calculate the heat needed to increase the temperature of the system from $10°C$ to $90°C$.

For iron we have

$$Q_{iron} = mc_{iron}\Delta T = 20kg \cdot 0.01kcal \cdot (kg\ °C)^{-1} \cdot (90-10)°C = 176kcal \tag{6}$$

and for water

$$Q_{water} = mc_{water}\Delta T = 20kg \cdot 0.01kcal \cdot (kg\ °C)^{-1} \cdot (90-10)°C = 1600kcal \tag{7}$$

The total heat required is thus

$$Q_{total} = Q_{iron} + Q_{water} = 1776kcal \tag{8}$$

When the system cools down from $90C^\circ$ to $10C^\circ$, the heat going out from the system is $1776kcal$. Note that water is a good heat reservoir being a material with one of the highest value of c.

Why is the heat capacity so important? It connects two quantities which are easy to measure: Temperature change and heat added to the system (calorimetry).

So far, the specific heat, c, for solid and liquid is given by:

$$Q = mc\Delta T \tag{9}$$

where the heat Q is in cal, m is the mass in g and ΔT the temperature difference in degree Celsius.

For gas, two more variables, volume (V) and pressure (P), need to be considered. Therefore, two kinds of specific heats are introduced:

- c_v: specific heat at constant volume
- c_p: specific heat at constant pressure.

and they are fairly different as shown in Table 1 for different molecules.

Different Specific Heat	c_v	c_p	C_V	C_P	$C_P - C_V$	$\gamma = C_P/C_V$
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	0.350	0.482	6.20	8.20	2.00	1.32

Table 1: Specific heats and molar specific heats of various substances.

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

$$N_A = 6.02 \times 10^{23} \tag{10}$$

N_A is the Avogadro number. Related C_V and C_P are called *molar* Specific Heats. The heat needed to raise the temperature of n moles of gas, i.e. with $n \times N_A$ molecules, by ΔT in $^\circ C$ is given by

$$\begin{aligned} Q_V &= nC_V\Delta T \text{ at constant volume} \\ Q_P &= nC_P\Delta T \text{ at constant pressure} \end{aligned} \tag{11}$$

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

$$\begin{aligned} C_V &= r\ c_v \\ C_P &= r\ c_p \end{aligned} \tag{12}$$

By noting that the atomic mass of the He, Ne, N_2 etc. are given by $\sim$ 4 u, $\sim$20 u, $\sim$28 u, etc., respectively, Table 1 shows that this relation is indeed valid.
Let's now heat ideal gas very slowly at

1. constant volume V, or
2. constant pressure P,

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

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

$$\Delta E_{int} = Q_V = nC_V \Delta T \tag{13}$$

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

$$C_V = \frac{1}{n}\left(\frac{\Delta E_{int}}{\Delta T}\right)_{V=constant} \equiv \frac{1}{n}\left(\frac{\partial E_{int}}{\partial T}\right)_V \tag{14}$$

The process 2. requires

$$\Delta E_{int} = Q_P - W \tag{15}$$

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

$$Q_P - Q_V = W = P\Delta V \tag{16}$$

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

$$\Delta V = \frac{nR\Delta T}{P} \tag{17}$$

leading to

$$Q_P - Q_V = P\frac{nR\Delta T}{P} = nR\Delta T \tag{18}$$

Combined with $Q_P = nC_P\Delta T$ and $Q_V = nC_V\Delta T$, it follows that

$$C_P - C_V = R \tag{19}$$

i.e. $C_P > C_V$, more heat is needed at constant pressure (than at constant volume) to raise the temperature by the same amount to compensate the work done at the same time.
Also note that the gas constant is given by

$$R = 8.314\frac{J}{mol\ K} = 1.99\frac{cal}{mol\ K} \tag{20}$$

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

6.3 Heat capacity for non-ideal gas and equipartition theorem

For ideal gas we assume atoms/molecules with only translational kinetic energy, but no angular momentum, no vibrational degrees of freedom. In this section, we consider these additional degrees of freedom for the kinetic energy E_{kin}.

Equipartition of Energy
In the kinetic theory of point-like ideal gas, discussed in Chapters 4 and 5, we obtained

$$PV = Nm\langle v_x^2 \rangle = \frac{2}{3}N\left(\frac{1}{2}m\langle v^2 \rangle\right) = \frac{2}{3}N\langle K \rangle \tag{21}$$

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

$$E_{int} = \frac{3nRT}{2} \tag{22}$$

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

$$\Delta E_{int} = Q_V = nC_V \Delta T, \tag{23}$$

it follows that

$$C_V = \frac{1}{n}\left(\frac{\Delta E_{int}}{\Delta T}\right) = \frac{3}{2}R \tag{24}$$

Using the value of R, we obtain $C_V = 2.98 cal/(mol\ K)$, in a good agreement with monatomic gasses.

But let's now turn to higher-atomic gases with not only translational motions. We 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 is a function of variable x in the form of $E = \alpha x^2$ with a constant α. The average energy $\langle E \rangle$ is then given by

$$\langle E \rangle = \frac{\int_{-\infty}^{\infty} \alpha x^2 e^{-\alpha x^2/kT} dx}{\int_{-\infty}^{\infty} e^{-\alpha x^2/kT} dx} = \frac{kT}{2} \tag{25}$$

If we extend the energy to be

$$E = \sum_{i=1}^{n_f} \alpha_i x_i^2 \tag{26}$$

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

$$\begin{aligned} \langle E \rangle &= \frac{\int_{-\infty}^{\infty} dx_1 \cdots \int_{-\infty}^{\infty} dx_{n_f} \sum_{i=1}^{n_f} \alpha_i x_i^2 e^{-\sum_j \alpha_j x_j^2/kT}}{\int_{-\infty}^{\infty} dx_1 \cdots \int_{-\infty}^{\infty} dx_{n_f} e^{-\sum_j \alpha_j x_j^2/kT}} \\ &= \sum_{i=1}^{n_f} \frac{\int_{-\infty}^{\infty} dx_1 \cdots \int_{-\infty}^{\infty} dx_{n_f} \alpha_i x_i^2 e^{-\sum_j \alpha_j x_j^2/kT}}{\int_{-\infty}^{\infty} dx_1 \cdots \int_{-\infty}^{\infty} dx_{n_f} e^{-\sum_j \alpha_j x_j^2/kT}} \end{aligned} \tag{27}$$

Since all but one integral cancel between the numerator and denominator, we have

$$\langle E\rangle = \sum_{i=1}^{n_f} \frac{\int_{-\infty}^{\infty} dx_i \alpha_i x_i^2 e^{-\alpha_i x_i^2/kT}}{\int_{-\infty}^{\infty} dx_i e^{-\alpha_i x_i^2/kT}} = \frac{1}{2} n_f kT \tag{28}$$

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

$$\langle E\rangle = \frac{1}{2} n_f NkT, \text{ or } \langle E\rangle = \frac{1}{2} n_f nRT \tag{29}$$

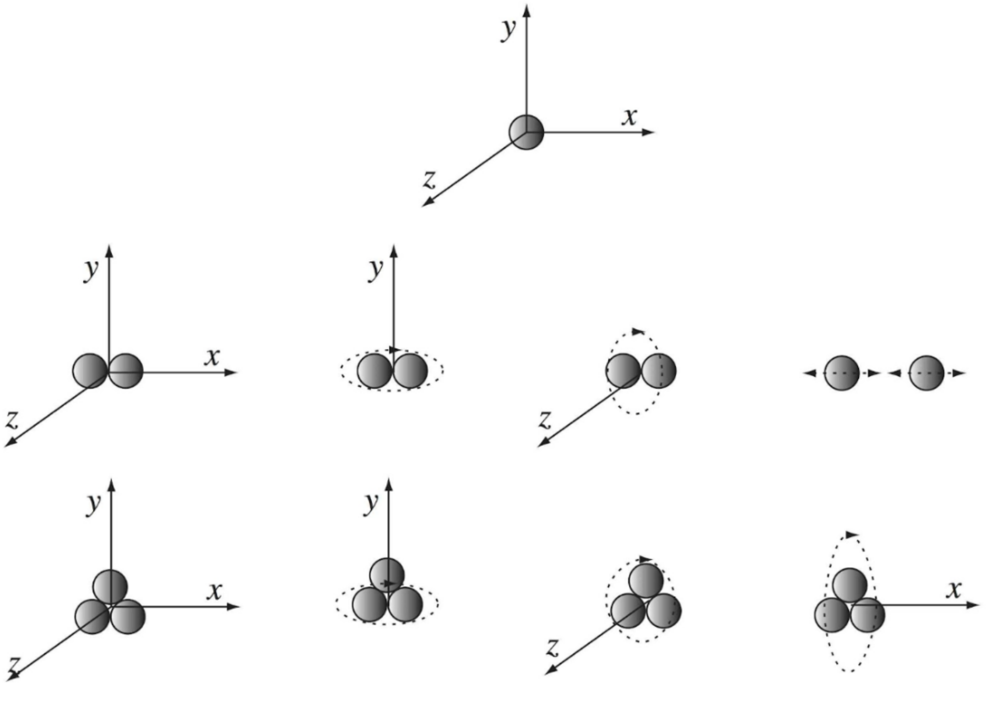
respectively. It follows that

$$C_V = \frac{1}{n}\left(\frac{\Delta E_{int}}{\Delta T}\right) = \frac{1}{2} n_f R \tag{30}$$

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

$$E = \frac{1}{2} m (v_x^2 + v_y^2 + v_z^2) \tag{31}$$

i.e. $n_f = 3$. More complex molecules have rotational and/or vibrational kinetic energy, in addition to the translational kinetic energy.



For example, diatomic or three-atomic molecules, if only considering rotational energy, have 5 or 6 degrees of freedom, i.e. $n_f = 5$ and 6, respectively:

$$E = \frac{m}{2}\left(v_x^2 + v_y^2 + v_z^2\right) + \frac{L_1^2}{2I_1} + \frac{L_2^2}{2I_2} \quad \text{and} \quad E = \frac{m}{2}\left(v_x^2 + v_y^2 + v_z^2\right) + \frac{L_1^2}{2I_1} + \frac{L_2^2}{2I_2} + \frac{L_3^2}{2I_3} \tag{32}$$

where L's are the angular momenta and I's corresponding moments. The energy of diatomic gas with additional vibrational motions is given by

$$E = \frac{1}{2}(v_x^2 + v_y^2 + v_z^2) + \frac{L_1^2}{2I_1} + \frac{L_2^2}{2I_2} + \frac{\mu}{2}(\dot{\vec{r}}_1 - \dot{\vec{r}}_2)^2 + \frac{k}{2}(\vec{r}_1 - \vec{r}_2)^2 \tag{33}$$

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: plus 1-vibrational kinetic and 1-vibrational potential energies, $n_f = 7$

With this derivation, we showed that (i) the energy of a molecule is equally shared among the active degrees of freedom and (ii) each degree of freedom carries on average $kT/2$ of the energy. **This is called the equipartition theorem.**

Note that

$$\frac{3}{2}R = 2.98 cal/mol \cdot K, \quad \frac{5}{2}R = 4.98 cal/mol \cdot K \quad \frac{7}{2}R = 6.97 cal/mol \cdot K \tag{34}$$

Measured values show that some of the degrees of freedom are not "active", and that the degrees of freedom may decrease with decreasing temperature to $n_f = 5$, then to $n_f = 3$ for different gas molecules, i.e. gases behave like monatomic molecules at very low temperatures. These observations/measurements are related to the foundation of quantum theory.

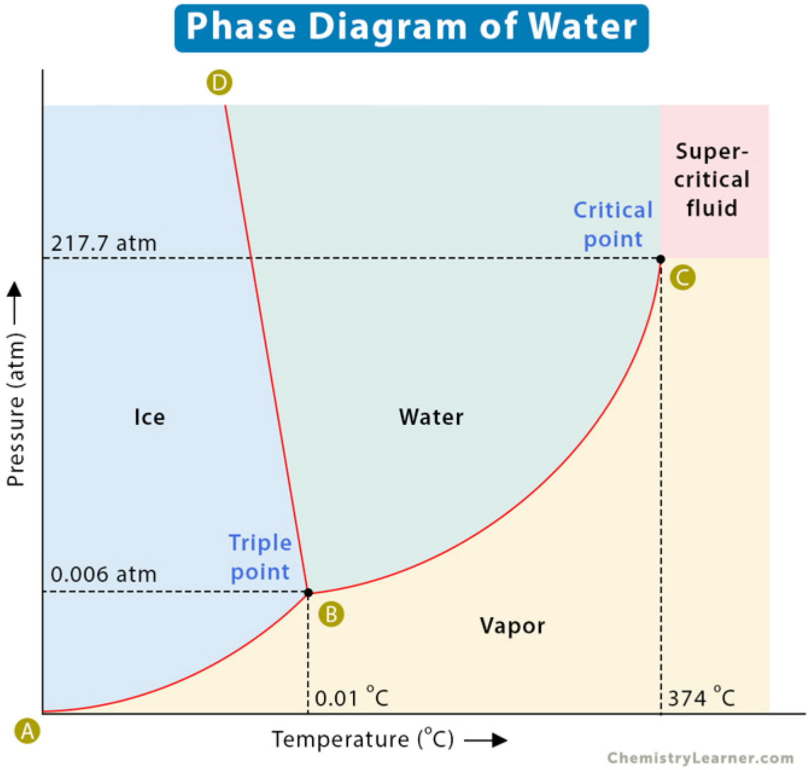
6.4 Latent heat and phase transitions

Phases of matter and transitions between them

As discussed in Chapter 1, there are three phases of matter: solid, liquid and gas. The table below summarises the transitions among these phases:

From/To	Solid	Liquid	Gas
Solid	-	Melting	Sublimation
Liquid	Freezing	-	Vaporization
Gas	Deposition	Condensation	-

Then, the Figure below is called "phase diagram" (here shown for water), where the areas of three phases are indicated as a function of pressure and temperature. When the solid black lines are crossed by changing the pressure or/and temperature, there is a phase transition, usually involving latent heat. At the triple point, all three phases exist simultaneously. Above critical point, vapour can change to water or water to vapour smoothly without latent heat.



Latent Heat

Latent heat is a form of heat that does not lead to a change in temperature. When the phase of matter changes, e.g. from solid to liquid, or from liquid to gas, heat needs to be added tot the system. However, the temperature of the system remains constant, i.e. all the energy is used to transform the molecular structure and not to increase the kinetic energy of the molecules:

- Specific latent heat of fusion (melting) L_F: heat needed to change 1 kg of material from the solid to liquid phase.
- Specific latent heat of vaporization (boiling) L_V: heat needed to change 1 kg of material from the liquid to gas phase.

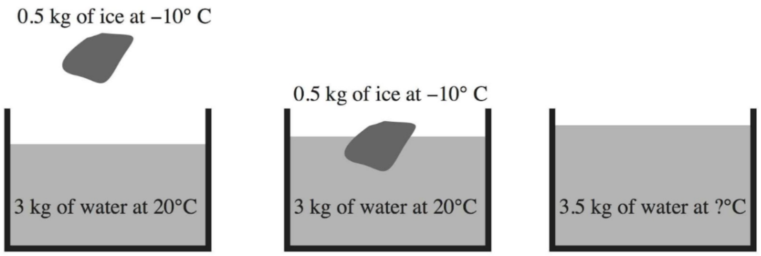
The total heat needed, Q, to melt m kg of material is then

$$Q = mL_F \tag{35}$$

On the other hand, in order to solidify m kg of liquid, $Q = mL_F$, must be taken out from the system at the melting temperature.

Example:

Let's consider a block of ice of 0.5 kg at $-10°C$ to be put into 3 kg of water at $20°C$. The specific heat of ice is $0.5kcal/(kg\ °C)$ and the specific heat of fusion, $79.7kcal/kg$.



For the ice to melt, first the temperature must raise to $0°C$ requiring a (sensible) heat of

$$Q_{ice} = mc_{ice}\Delta T = 0.5kg \cdot 0.5kcal(kg \cdot C^\circ)^{-1}(0+10)C^\circ = 2.5kcal \tag{36}$$

plus latent heat of

$$Q_{melting} = mL_F = 0.5kg \cdot 79.7kcal\ kg^{-1} = 39.85kcal. \tag{37}$$

Thus the total heat needed is

$$Q_{total} = Q_{ice} + Q_{meelting} = 42.35kcal \tag{38}$$

which has to be taken from the 3 kg of water at $20°C$. This will cool down the temperature of the water to $T_{water-3kg}$, which can be derived from

$$-Q_{total} = mc_{water}\Delta T = 3kg \cdot 1kcal(kg \cdot C^\circ)^{-1}(T_{water-3kg} - 20)C^\circ = -42.35kcal \tag{39}$$

leading to

$$T_{water-3kg} = -\frac{42.35kcal}{3kcal \cdot C^{\circ -1}} + 20C^\circ = 5.88C^\circ \tag{40}$$

Now we are putting 3kg of water at $5.88°C$ and 0.5 kg of water at $0°C$ together. If we denote the final temperature of 3.5 kg of water to be $T_{water-3.5kg}$, the heat needed for the 0.5 kg of water is

$$Q_{0.5kg} = mc_{water}\Delta T = 0.5kg \cdot 1kcal(kg\ °C)^{-1}\ (T_{water-3.5kg} - 0)°C \tag{41}$$

and heat of 3kg of water is

$$Q_{3kg} = mc_{water}\Delta T = 3kg \cdot 1kcal(kg\ °C)^{-1}\ (T_{water-3.5kg} - 5.88)°C \tag{42}$$

Since they are mixed each other,

$$Q_{0.5kg} + Q_{3kg} = 0 \tag{43}$$

leading to

$$0.5kcal\ T_{water-3.5kg} + 3kcal\ T_{water-3.5kg} - 3kcal \times 5.88 = 0 \tag{44}$$

Thus, we obtain:

$$T_{water-3.5kg} = \frac{3kcal\ \times 5.88C^\circ}{0.5kcal\ + 3kcal} = 5.04°C \tag{45}$$

i.e. the temperature of the water becomes $5.04°C$.

Evaporation and boiling

At the boiling point, liquid changes to gas everywhere leading to the formation of gas bubbles in the liquid. On the other hand, the change from liquid to gas occurs at the boundary surface between the two even below the boiling temperature, called evaporation: molecules with higher kinetic energy escaping from the liquid phase to the gas phase. Thus, the average kinetic energy of the molecules remaining in the liquid decreases, thus the temperature of the liquid drops.