Principles of Physical Chemistry   2023

prof. Kari Laasonen, Department of Chemistry and Materials Science, office C221b, kari.laasonen@aalto.fi

The course will follow mostly the Engel and Reid book Physical Chemistry 4th edition (Part 1, Thermodynamics), which is available in the Pearson web page.

See instructions how to login to the book from the MyCourse course 'Practical issues' folder

The course will cover chapters 1-9 (Thermodynamics) and 18-19 (Chemical Kinetics)

This material is in the MyCourse page.

 There will also be exercises and quizzes in the course.

Thermodynamics

Thermodynamic is the field of chemistry that study equilibrium processes. This is important since all systems are in or **close to equilibrium**.

E. Bauer formulated the *Universal Law of Biology*: "All and only living systems are never in equilibrium and perform constant work at the expense of their free energy against the equilibrium required by the laws of physics and chemistry under existing external conditions".

Liquid water is in equilibrium with water vapor or at lower temperatures with ice. All water in the atmosphere comes from evaporation of liquid water. In clouds gas phase water condense to small (cloud)droplets which may rain down.
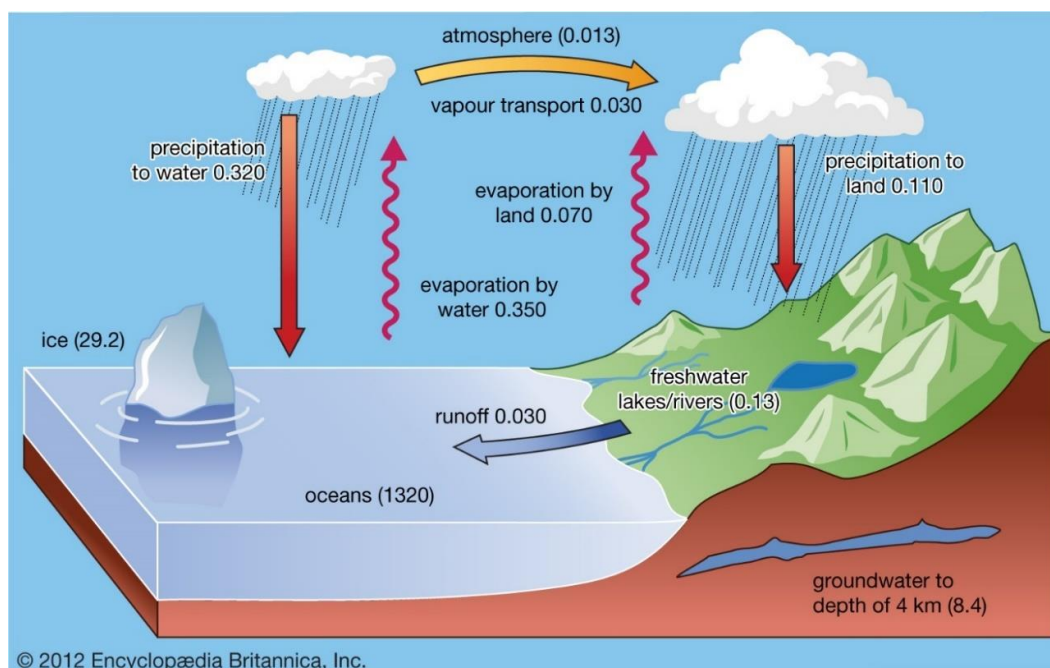

Figure 1: The numbers refer to the amount of water.

Every chemical process is close to equilibrium and the **equilibrium of the process** will depend on the environment, like temperature and pressure. In real life (like in atmosphere or inside a body) the temperature, pressure or concentrations change continuously. In addition, thermodynamics will not tell how long the equilibration will take. We will examine also chemical kinetics which is the theory of the rate of reactions.

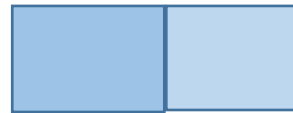A + B <-> AB   K = [AB]/[A][B]   K is the equilibrium constant
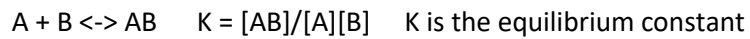
Applications:

Methane (CH_4), n-hexane (C_6H_{14}, a model for gasoline) and coal (mostly graphite) can be used as fuels (in burning process).

Which produces most heat (enthalpy) per CO_2 molecule.

liquid-gas co-existence

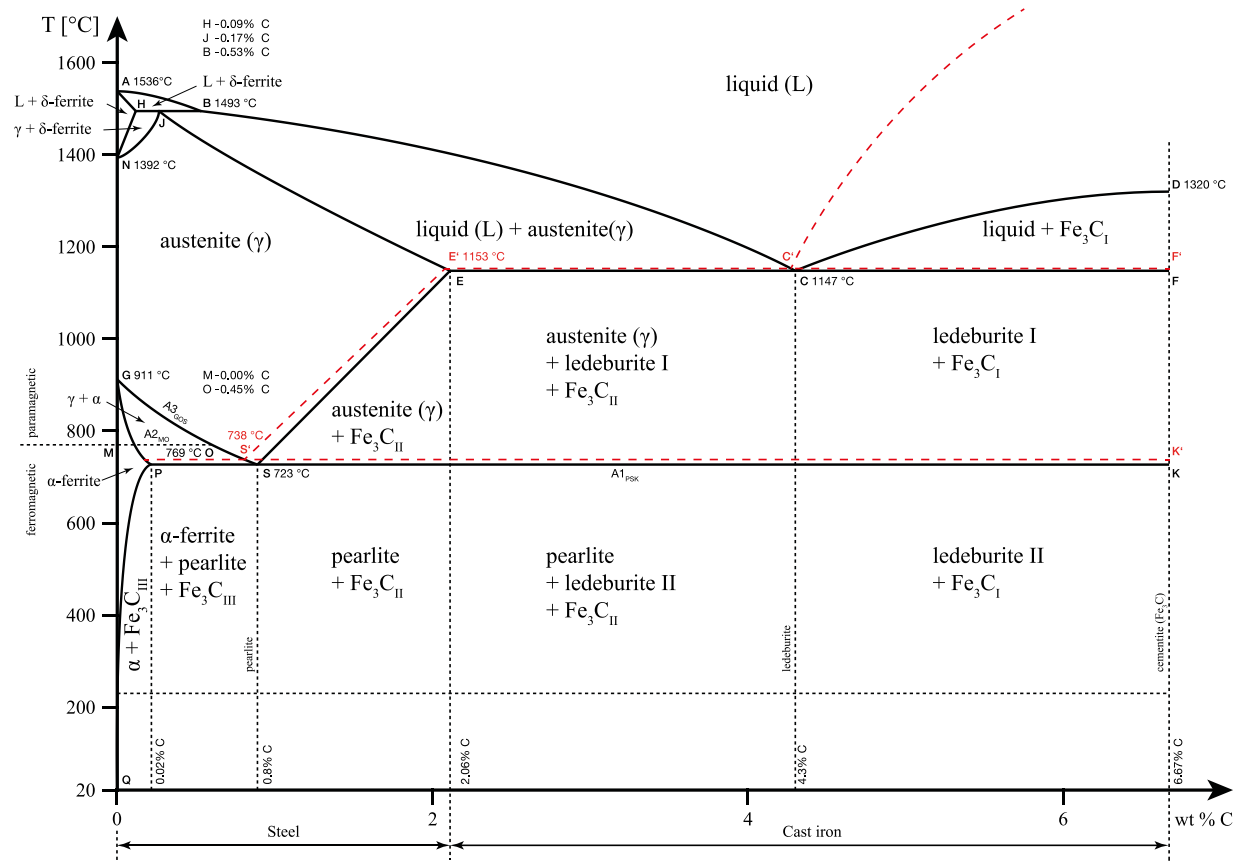low temperature (darker means higher density)   high temperature

All biochemical processes are connected to thermodynamics.

Example: ATP-ADP cycle (Adenosine tri/diphosphate), the main short term energy source in biological systems.

Phase diagrams help to understand how material is distributed. It is a map of possible phases some material can have. Different phases have different (mechanical) properties. Example: FeC phase diagram.

T [°C]

H -0.09% C
J -0.17% C
B -0.53% C

1600

A 1536°C — L + δ-ferrite
L + δ-ferrite
H — B 1493 °C
γ + δ-ferrite
J
1400
N 1392 °C

liquid (L)

D 1320 °C

austenite (γ)

liquid (L) + austenite(γ)

1200

E' 1153 °C
E
C'
C 1147 °C

liquid + Fe$_3$C$_I$

F'
F

1000

G 911 °C
M -0.00% C
O -0.45% C

austenite (γ)
+ ledeburite I
+ Fe$_3$C$_{II}$

ledeburite I
+ Fe$_3$C$_I$

γ + α
800
A3$_{GOS}$
A2$_{MO}$
769 °C O
738 °C
S'
austenite (γ)
+ Fe$_3$C$_{II}$

paramagnetic

M
P
S 723 °C
A1$_{PSK}$
K'
K

600
ferromagnetic
α-ferrite

α-ferrite
+ pearlite
+ Fe$_3$C$_{III}$

pearlite
+ Fe$_3$C$_{II}$

pearlite
+ ledeburite II
+ Fe$_3$C$_{II}$

ledeburite II
+ Fe$_3$C$_I$

400
α + Fe$_3$C$_{III}$

pearlite
ledeburite
cementite (Fe$_3$C)

200

Q
0.02% C
0.8% C
2.06% C
4.3% C
6.67% C

20
0
2
4
6
wt % C

Steel
Cast iron

Thermodynamics applies to all systems, and it will also set limits to all chemical processes, which **cannot be broken** how smart processes or catalyst we use. Usually, we are not at the thermodynamical limits since friction and other imperfect processes limit the system.

The thermodynamics will determine the efficiency of all thermal **energy processes**. It explains why the gasoline engine have maximum efficiency of ca. 35 % but electrical engines have efficiency close to 100 %.

Thermodynamics can be applied to continuous material (like water, ethanol, iron-carbon system) or to group of molecules of the same material. This is convenient since all material consist of molecules and we can choose the most convenient point of view. In this course **we mostly focus on the continuous material.**

We can derive the ideal gas law from very simple concepts of molecular collisions.

When a molecule with velocity v and with x-component with v_x collide to the container wall it will give a momentum, p, of $2mv_x$ to the wall. This will also create a force to the wall. $F=ma$

Area = A
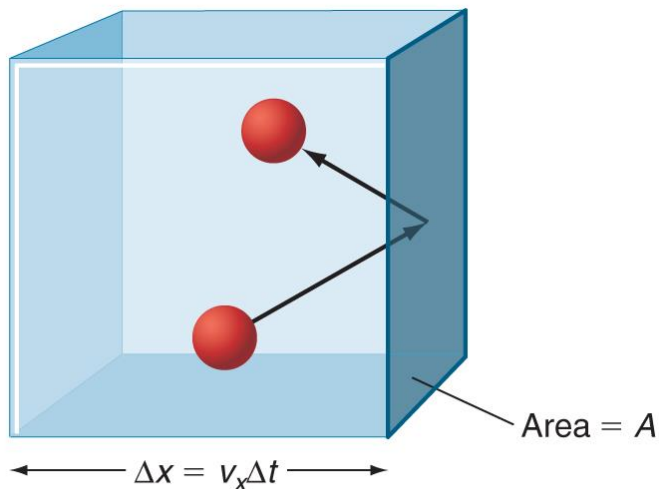
$\Delta x = v_x \Delta t$

© 2013 Pearson Education, Inc.

$a = \frac{dv}{dt} = 2v_x/\Delta t$ for each collision so $F = 2mv_x/\Delta t$ but how many collisions there are in a second. This depends on the density of the system. The molecules from $\Delta x = v_x \Delta t$ from the wall can collide to the wall within Δt if the velocity is towards the wall. The area of the surface is A and the number of molecules in the $A\Delta x$ volume is $A\Delta x\rho$, where $\rho_N = N/V$ is the gas number density (not the mass density or density). The molecules v_x velocity can be either towards or away from the surface so only half of the molecules will collide so

$$N_{coll} = \frac{1}{2}\rho_N \, A \, v_x \Delta t$$

and the force is

$$F = 2mv_x N_{coll}/\Delta t = m \, \rho_N \, A \, v_x^2$$

and the pressure (note that $E_{kin} = \frac{mv^2}{2}$ and $v^2 = v_x^2 + v_y^2 + v_z^2$

$$P = \frac{F}{A} = \rho_N m v_x^2 = \rho_N 2/3 * E_{kin}$$

The molecules kinetic energy is related to temperature. We do not proof it here but $E_{kin} = 3k_bT/2$ where k_b is the Boltzmann constant. So

$$P = \rho_N \, k_b T = \frac{Nk_bT}{V} = \frac{nN_Ak_bT}{V} = \frac{nRT}{V}$$

here the R is ideal gas constant. The temperature here is in Kelvins. This equation does not depend on the type of gas used. The ideal gas equation can be used to estimate the absolute zero temperature. Here the pressure of dilute gas is measured in fixed volume on different temperatures.
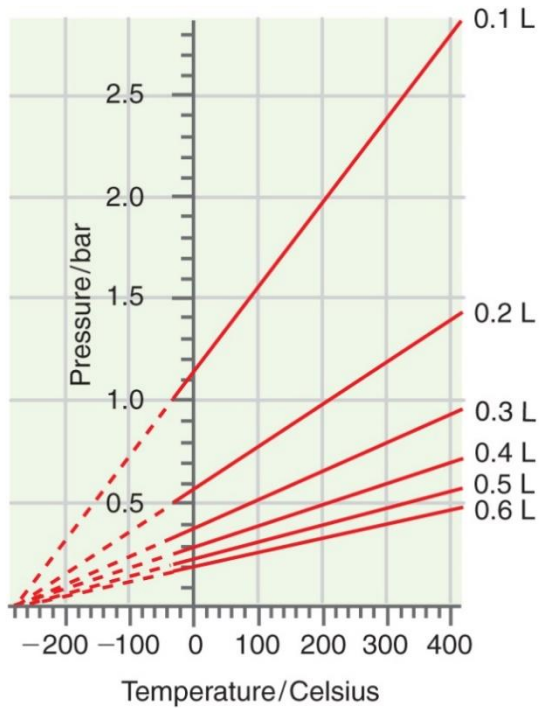
Some definitions of Thermodynamics   Engel & Reid chapter 1.3

The key concept in thermodynamics is that systems need to be in equilibrium with respect of some variable like **pressure P, temperature T, volume V and particle number N** (or concentration). Some of them (P,T,V,N) or total energy E can/should be constant.

Two different systems can be in thermal equilibrium if they can change **energy**, case (c). If the systems have insulating walls, they can be in contact but the temperature is different, case (b). The case (b) is called **adiabatic**. Here we assume that the containers have the same volume and number of gas molecules. The meter can indicate the pressure or temperature of the system.
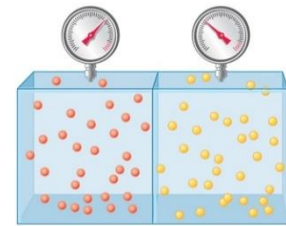
Zeroth law of thermodynamics:

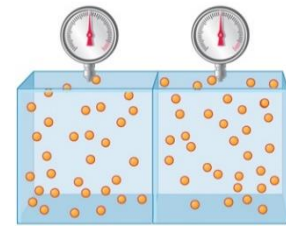*If two systems are separately in thermal equilibrium with a third system, they also are in equilibrium.*
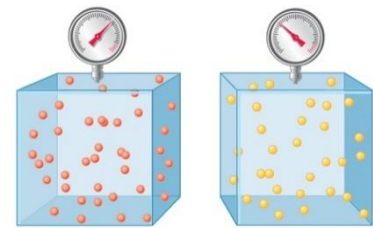
(a)

(b)

(c)

© 2013 Pearson Education, Inc.

Intensive and extensive variables   Engel & Reid chapter 1.4

All thermodynamical variables are either intensive – they do not depend on the **system size** – or extensive – they depend on the system size. Pressure P and temperature T are intensive whereas volume V and particle number N are extensive. If a thermodynamical equation, have extensive variable on the left side also on the right side need to be an extensive variable.

$$P = \rho_N \, k_b T = \frac{k_b NT}{V} = \frac{nRT}{V}, \quad PV = k_b NT = nRT$$

Partial pressures

Almost always the systems contain several different gases or molecules, so does the ideal gas pressure depend on the different molecules? Answer: No. The total pressure is the sum of the pressure of each molecule type.

$$P = \sum_i P_i \; ; \; P_i = n_i RT$$

here the P_i are the partial pressures of each gas and n_i are the molecular density of each type of gas. One can also define the mole fraction as $x_i = n_i/n$.

Examine the Problem 1.2

What are the final pressure and partial pressures when the separating walls have been removed? The temperature is fixed to 298.15 K.

He	Ne	Xe
2.00 L	3.00 L	1.00 L
1.50 bar	2.50 bar	1.00 bar
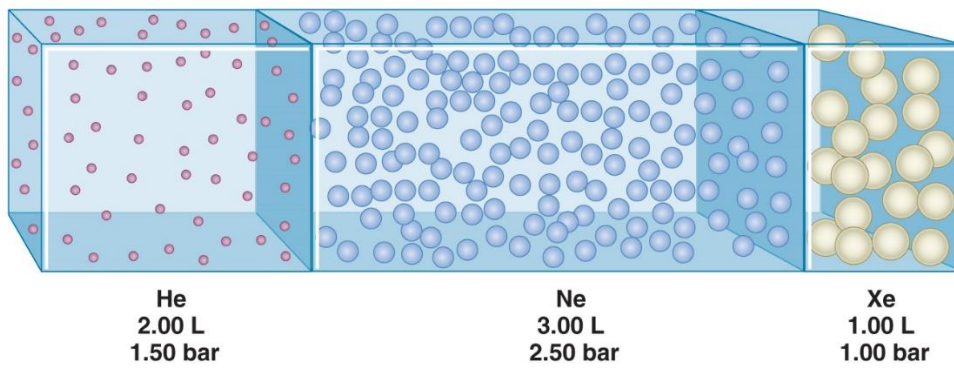
There is a quiz of this.

The ideal gas is an idealization since all molecules will interact and they have some size. This can be seen in several experiments. E.g. in the estimation of the absolute zero temperature. At finite pressures the estimation differs from one gas to another. Note these are very weakly interacting gases with low boiling points.

One can sketch a qualitative molecule-molecule interaction curve. When the molecules are far away ($r_{transition}$) they do not interact and this the case in dilute gases. When they get closer there is an attractive part up to distance r(V=0) and then the interaction become repulsive. This interaction model is schematic and the details differ from molecule to molecule.

Question: which is more ideal gas – water vapor or Argon. Why?

There is a quiz of this.

The molecular interactions will modify the ideal gas law and there are several different real gas laws. One of the often used is the van der Waals equation

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

where a and b are gas dependent parameters. There are quite many of them listed in Table 7.4. The parameter b is related to molecules volume and it will increase the pressure. The a is related to the attractive interaction. The second term is negative and thus it reduce the pressure. The parameters a and b are empirical.

Examine the Problem 1.4

For N_2 the vdW parameters are a = 1.37 bar dm^6 mol^{-2} and b = 0.0387 dm^3 mol^{-1} . Compute the pressure at 300 K, for 1 mol of gas and V = 250 L and 0.1 L. Note that in the book example the molar volume V_m is given. This is the volume 1 mol of gas will take. The final results are the same.

Answer: at V= 250 L, ideal gas: P= 9.98*10^{-2} bar, vdW: P = 9.98*10^{-2} bar (almost no difference)

at V = 0.1 L, ideal gas: P= 249 bar, vdW: P = 270 bar (high pressure and rather big difference, vdW predict higher pressure)
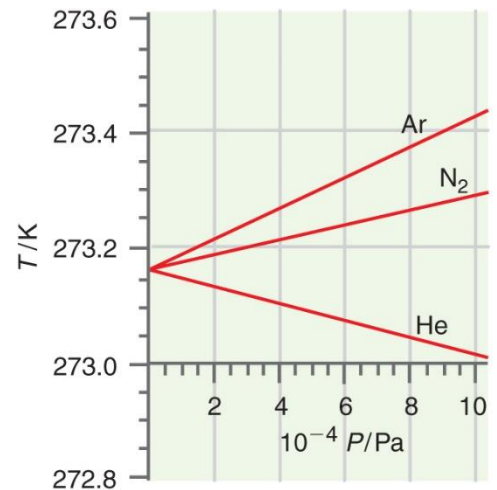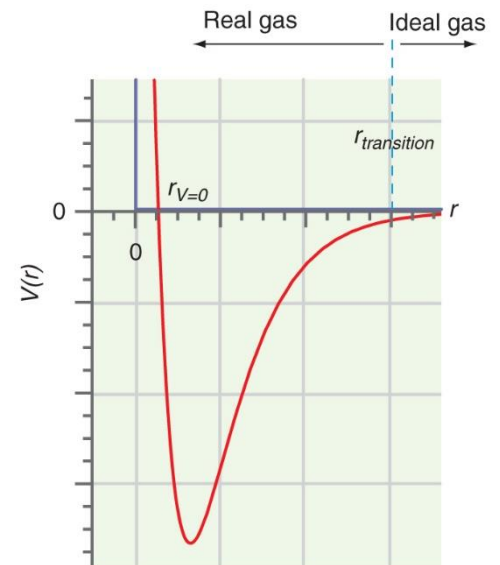
If the molecules are infinitely small and they do not interact (ideal gas) the system cannot be in equilibrium. Put 0.5 mol of molecules with temperature of 1 K and 0.5 mol of molecules with temp. of 599 K in an ideal box (of 24.79 L). The pressure is 1 atm and average temperature is 300 K but the hot molecules remain hot and cold molecules cold.

Internal Energy and First Law of thermodynamic chapter 2.1	Engel & Reid

Energy is a fundamental quantity in many chemical systems. In thermodynamics, there are several energies. We start with the **Internal Energy U**. U contains all possible energy forms of the molecules. These include the

- kinetic energy
- molecular interactions
- possible bond energy, important if some chemical reactions happen.
- rotation and vibration energy

The distribution of energies in U can vary but in a closed system U cannot change. In equilibrium each degree of freedom (kinetic, rotation and vibration) will have the same amount of energy.
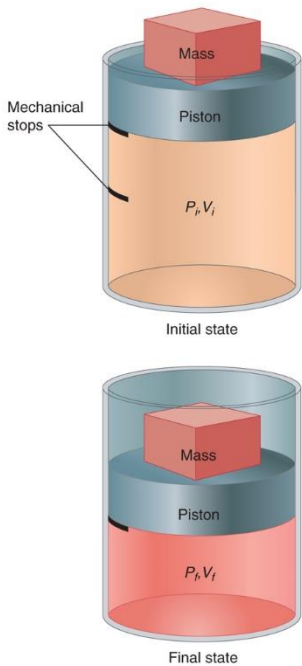
This is **the first law of thermodynamics**

In isolated system, the internal energy U is constant

The internal energy can be divided to U_{system} and $U_{environment}$. For an isolated system ΔU_{system} = - $\Delta U_{environment}$. We are mostly interested of the system and subindex is usually leaved out.

Initial state

Final state

© 2013 Pearson Education, Inc.

If some **work w** is introduced to a system, it will change the **heat q**. The internal energy is a sum of these

$$\Delta U = q + w$$

If we compress an isolated container with weight M with distance x the work is

$$w = \int_{x_1}^{x_2} F.\,dx = Mgx$$

for isolated system $\Delta U = 0$ so the heat is w=-q

We can also compute the work when the system volume change in constant pressure (P_{ext})

$$w = -P_{ext} \int_{V_1}^{V_2} dV$$

Usually the pressure depend on volume, ideal gas $P(V) = nRT/V$

$$w = -\int_{V_1}^{V_2} P(V)dV$$

A more complex example with electrochemical water splitting reaction. This is more complex since the current will produce gases, H_2 and O_2. All the work put into the system will go to the chemical reaction and expansion. Note that the piston with mass will increase.

Initial state

Final state
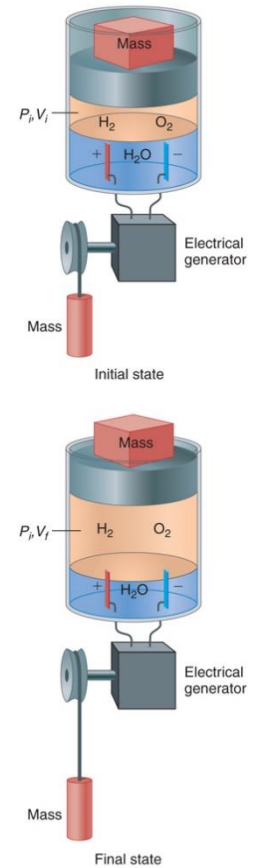
© 2013 Pearson Education, Inc.

Examine the Problems 2.1 and 2.2

One mol of ideal gas is expanding slowly from V to 2V at constant temperature (300K). What is the work?

$$w = -\int_{V_1}^{V_2} P(V)dV = -nRT \int_{V_i}^{V_f} \frac{dV}{V} = -nRT \ln\frac{V_f}{V_i} = -nRT * \ln 2 = -1.73\ kJ$$

One mol of ideal gas is held under a piston at pressure $2.0*10^4$ Pa then the pressure is reduced to half $1.0*10^4$ Pa. The system expands at constant temperature (300K). What is the work?

Now P = const = $1.0*10^4$ Pa. Initial volume (20 kP) is V=nRT/P=0.125 m³, final volume = 0.25 m³.

$$w = -P_{ext} \int_{V_1}^{V_2} dV = -10^4 Pa\ (0.25 - 0.125)m^3 = -1.25\ kJ$$

The work is different even the volume change is same. Reason – different process.

Heat	Engel & Reid chapter 2.2

The heat is a bit abstract object but it mostly correspond to that what is commonly considered as heat.

- The heat only appears during the change of state
- The net effect of heat is to change the internal energy of the system.
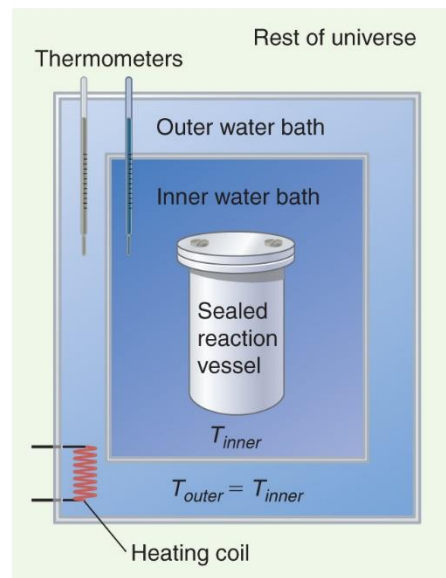- The heat flow from hot to cool. If the system is heating the q is positive and vice versa.

Examine the Problems 2.4

You heat 100 g of water in an isolated system at 1 bar pressure with a coil with 2 A current and 12 V for 1000 s. Then 10 % of the water has evaporated. The temperature is 100 °C and the densities of water and gas is 997 and 0.590 kg/m^3.

The work done by the coil is q = IUt = 24.0 kJ the expansion work is -1.70 kJ.

Where has the extra energy gone?

There is a quiz of this.

Rest of universe
Thermometers
Outer water bath
Inner water bath
Sealed reaction vessel
T_{inner}
$T_{outer} = T_{inner}$
Heating coil

© 2013 Pearson Education, Inc.

The heat capacity is the ability of the system to store heat (or energy). When energy is added to the system its temperature increases

$$C = \lim_{T \to 0} \frac{q}{T_f - T_i} = \frac{dq}{dT}$$

The heat capacity depends on the systems. For example, water have high heat capacity whereas gases have very low one. The C also depends on the experimental conditions. If the pressure P or volume V is kept constant where have two different heat capacities, C_V and C_P. Often the molar C is used, so the C is divided by the amount of material, it symbol is C_m (and also $C_{P,m}$ and $C_{V,m}$). Some values of $C_{P,m}$ are given in Appendix A Tables 2.3 and 2.4.

On the left, there are heat capacities of some gases at different temperatures. Note that the values change quite a lot (except for He). Read the explanation form the textbook.

The heat capacity depends on the degrees of freedom (dof) of the molecules. He has only translation dof (3 dof) and each atom have (kinetic) energy of $3k_bT/2$ then the molar heat capacity of He is 3R/2 = 12.472 J/(K mol). CO molecule can also rotate (linear molecule, over x- and y-axis, 2 dof) but at low temperatures the vibrations are not active so CO have $C_{V,m}$ = 5R/2 = 20.785 J/(K mol).). CO_2 molecule is linear and it rotates (2 dof). The bending vibration is rater soft and it has some contribution at 200 K, $C_{V,m} \approx 6R/2$ = 24.94 J/(K mol).
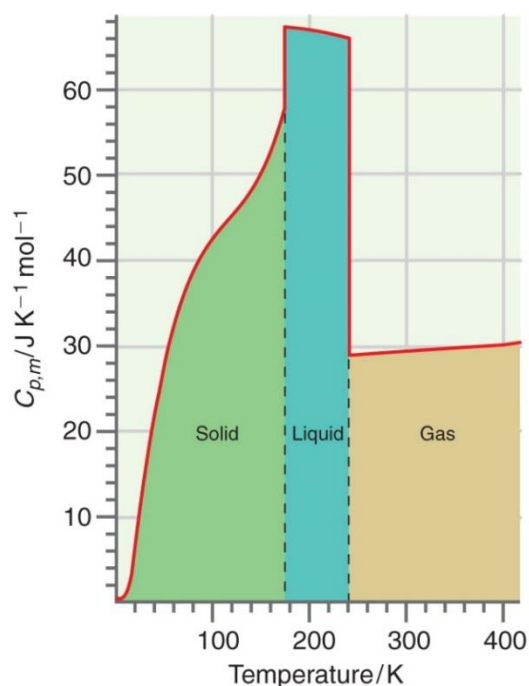
The heat capacity can be measured of any system. Below is the $C_{P,m}$ for Cl_2. The higher $C_{P,m}$ for solid and liquid is due to molecular interactions. Note: the sharp changes at the phase transitions.

The $C_{P,m}$ and $C_{V,m}$ are related. In dilute gases $C_{P,m} = C_{V,m} + R$

As comparison, water (liquid, 298.15 K) $C_{P,m}$ = 75.3 J/(K mol), (gas, 298.15 K) $C_{P,m}$ = 33.6 J/(K mol), $C_{V,m}$ = 25.3 J/(K mol).
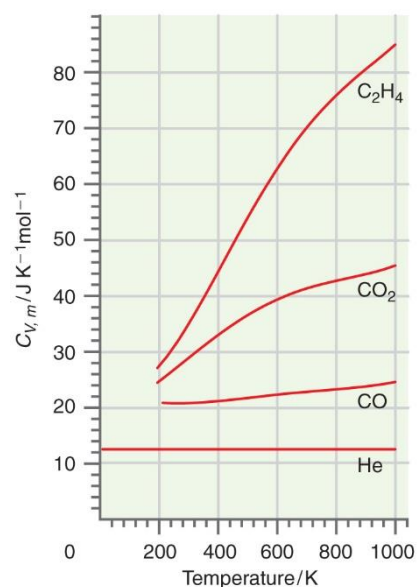
© 2013 Pearson Education, Inc.

© 2013 Pearson Education, Inc.

So called state functions are very useful in thermodynamics. They **depend only on the initial and final values of the system** not how we get there. Importantly the internal energy U is a state function.

$$\Delta U = \int_i^f dU = U_f - U_i$$

That is simple but the work, w, and heat, q, are not state functions. They depend how the system has been changed.

Let's look the examples 2.1 and 2.2 We start with container that has gas at pressure P_1, volume V_1 and temperature T_1. When this is compressed to P_2, V_2 and T_2 the work done is

$$w = -\int_{V_i}^{V_f} P_{ext} dV = P_{ext} \, \Delta V$$

by varying the mass on top of the piston we can modify the P_{ext} so the work depend on the mass or the procedure we choose. Work (and heat) are not state functions, they are called path functions. If we know w in the process we can compute the heat as

$$q = \Delta U - w = \Delta U + P_{ext} \, \Delta V$$
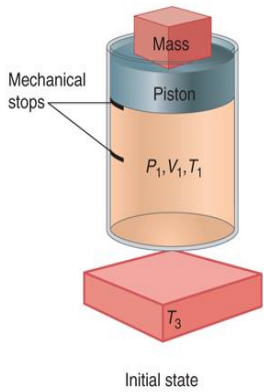
This is an important example of the thermodynamical processes. We look a constant temperature compression cycle. The container is assumed to be part of large temperature reservoir and it's temperature is always constant.

Let us look fist the irreversible cycle. We start at T_1, P_1, and V_1, then the pressure is rapidly reduced to P_2, and then the volume will expand to V_2. (The temperature is constant, $T_1 = T_2 = T$). (Note that the left and right figures are conflicting.)

Then at P_2, V_2 the pressure is rapidly changed to P_1, and the volume will compress back to V_1.

The work done in expansion is $-P_2 \Delta V = -P_2(V_2 - V_1)$ and in the compression $-P_1 \Delta V = -P_1(V_1 - V_2)$ and the total work is

$$w_{tot} = w_{exp} + w_{comp} = -(P_2 - P_1)(V_2 - V_1) > 0$$

because the process is cyclic (the initial and final states are same) $\Delta U = 0$ and the total heat is $q_{tot} = -w_{tot}$.

In the **reversible** process the pressure change is slow and $P = P_{ext}$. For ideal gas we can compute the expansion work
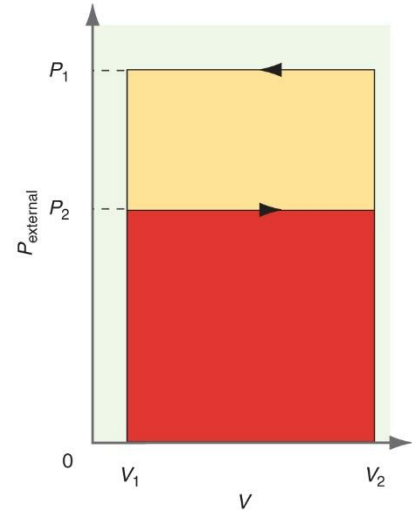
$$w_{exp} = -\int_{V_1}^{V_2} P_{ext}\, dV =$$

$$-nRT \int_{V_1}^{V_2} \frac{dV}{V} = -nRT \ln\frac{V_2}{V_1}$$

and similarly for the compression work

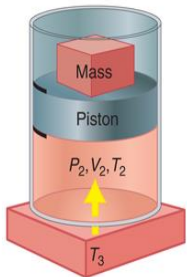$$w_{comp} = -nRT \ln\frac{V_1}{V_2}$$

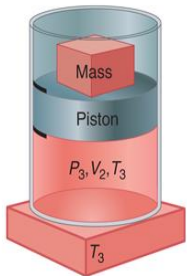Now the $w_{comp} = -w_{exp}$ and $w_{tot} = 0$. Also $q_{tot} = 0$

The example problem 2.4. illustrates the differences of the reversible and irreversible processes.

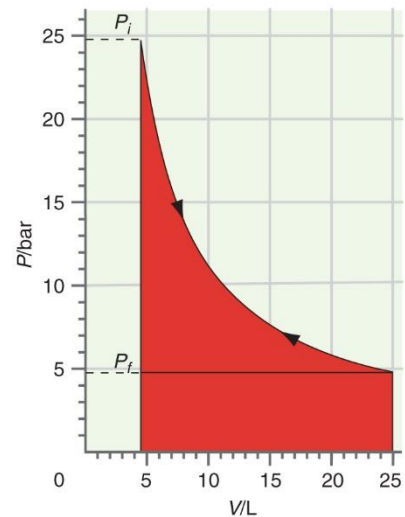Often in chemical systems (reactions) the change in energy is important. How can we measure the energy. If the process is at constant volume the work = 0, $w = -\int P_{ext}\, dV = 0$ and then the

$$\Delta U = q_v$$

The q can be measured from the heat flow of the system. The problem is that usually it is difficult to keep the system in constant volume. The pressures may become high. A more natural control variable is pressure. (Like in normal lab conditions.)

Now the change in internal energy at constant pressure is

$$\Delta U = \int_i^f dU = U_f - U_i = \int_i^f dq_P - P \int_i^f dV = q_P - P(V_f - V_i)$$

we can rearrange them a bit,

$$U_f + PV_f - (U_i + PV_i) = q_P$$

now we can define a new "energy" the **enthalpy**

$$\boxed{H = U + PV}$$

The enthalpy is the relevant energy in the constant pressure case and that is usually reported in chemical reactions. When we define a reaction endo- or exothermic we refer to the enthalpy. Enthalpy is one of the key quantities in thermodynamics. It is a state function.

In everyday life enthalpy is connected to heat. If an exothermic reaction happens the system heats. If we heat a system we increases its enthalpy.

Internal energy, Enthalpy and Heat capacity   Engel & Reid chapter 2.10

For ideal gas the internal energy and enthalpy can easily be formulated with the heat capacity:

In constant volume system:

$$\Delta U = q_v = C_V(T_f - T_i)$$

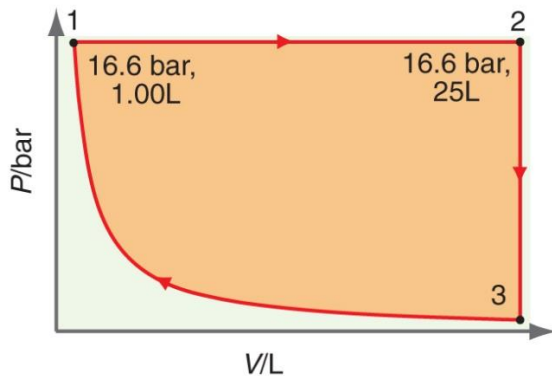For ideal gas this holds also for non-constant volume systems.

In constant pressure systems.

$$\Delta H = q_P = C_P(T_f - T_i)$$

For ideal gas the two heat capacities have simple relation

$$C_P - C_V = nR$$

© 2013 Pearson Education, Inc.

Compute q, w, ΔU and ΔH of the different segments of the cycle. There is 2.5 mol of ideal gas which have $C_{V,m}$ = 20.79 J/(mol K). The ideal gas law holds on the curved path, T = T_1 =T_3. R = 0.083144 L bar/(K mol)

what are the total q, w, ΔU and ΔH over the cycle.

Path 1 -> 2: P = const,

$$\Delta U = q_v = C_V(T_2 - T_1) = nC_{V.m}(T_2 - T_1) = 2.5\ mol\ 20.79\ \frac{J}{(mol\ K)}\ (1996 - 79.9)K = 99.62\ \text{kJ}$$

$$T_1 = \frac{P_1 V_1}{nR} = \frac{16.6\ bar\ 1\ L}{2.5\ mol\ 0.08314\ L\frac{bar}{K\ mol}} = 79.9\ \text{K},\quad T_2 = \frac{P_2 V_2}{nR} = \frac{16.6\ bar\ 25\ L}{2.5\ mol\ 0.08314\ L\frac{bar}{K\ mol}} = 1996\ \text{K}$$

work done $w = -P(V_2 - V_1) = -16.6\ bar * (25 - 1)L = -16.6 * 24 * 10^5 Nm^{-2} * 10^{-3} m^3 = -39.8\ kJ.$ (note 1 bar = $10^5 Nm^{-2}$ and L = $10^{-3} m^3$)

heat: $q = \Delta U - w = $ (99.6 + 39.8)kJ = 139.4 kJ.

enthalpy $\Delta H = \Delta U + \Delta(PV) = \Delta U + P\Delta V = $ (99.62 + 39.8)kJ = 139.4 kJ = q_p

We can also use the $C_{P,m}$ = $C_{V,m}$+R = (20.79 +8.314) J/(mol K) = 29.1 J/(mol K). $\Delta H = q_p = C_p(T_2 - T_1) = 2.5\ mol\ 29.1\ \frac{J}{(mol\ K)}\ (1996 - 79.9)K$ = 139.4 kJ.

Path 2 -> 3, V const, T_3 =T_1

$\Delta U = C_V(T_3 - T_2) = $ -99.79 kJ, $w = -P(V_3 - V_2) = 0$, $\Delta H = \Delta U + V\Delta P = \Delta U + nR\Delta T = $ $(-99.79 - 39.8)kJ = -139.6\ kJ$

Path 3 -> 1, T const

$\Delta U = C_V(T_1 - T_3) = 0$, $w = -\int P(V)dV = -nR\int \frac{dV}{V} = -nR \ln\left(\frac{V_1}{V_3}\right) = 5.35\ kJ$, $\Delta H = \Delta U + nR\Delta T = 0$, because $\Delta U = 0$ -> q = -w.

Total cycle

$\Delta U = 0$ and $\Delta H = 0$, w = -34.5 kJ, q = -w

This is a long one but important to go through. The table at the end of the example summarize the results

There is a quiz of this.

Reversible adiabatic expansion of ideal gas   Engel & Reid chapter 2.11

Adiabatic process: *q=0*

See also problem 2.8

In atmospheric conditions, the reversible adiabatic *q=0* processes are important. The air masses moves quite slowly and $P = P_{external} = \frac{nRT}{V}$.

The change of internal energy ΔU = w or on difference form $C_V dT = -P_{ext} dV = \frac{nRT}{V} dV$ => $\frac{C_V dT}{T} = nR \frac{dV}{V}$ and this can be integrated

$$-nR \int_{V_i}^{V_f} \frac{dV}{V} = \int_{T_i}^{T_f} C_V \frac{dT}{T}$$

if C_V is close to constant

$$-nR \ln \frac{V_f}{V_i} = C_V \ln \frac{T_f}{T_i} \quad => \quad (C_V - C_P) \ln \frac{V_f}{V_i} = C_V \ln \frac{T_f}{T_i} \quad => \quad (1 - \frac{C_P}{C_V}) \ln \frac{V_f}{V_i} = \ln \frac{T_f}{T_i}$$

we have used the relation C_P - C_V = *nR* (which is valid for ideal gas). We can define $\gamma = C_P/C_V$

$$\frac{T_f}{T_i} = \left(\frac{V_f}{V_i}\right)^{1-\gamma}, \quad \frac{T_f}{T_i} = \frac{P_f V_f}{P_i V_i} = \left(\frac{V_f}{V_i}\right)^{1-\gamma} \quad => \quad P_i V_i^{\gamma} = P_f V_f^{\gamma}$$

The equation provides convenient tool to estimate the P-V-T behavior in the adiabatic process.

Go through example 2.9

The initial temperature of the air at 2000 m is 288 K and pressure is 0.802 atm. It will rise adiabatically to 3500 m and pressure 0.602 atm. The $C_{P,m}$ of air is 28.86 J/(K mol) and $C_{V,m} = C_{P,m} - R$. What is the temperature at 3500 m.

Answer: 265 K (below freezing)