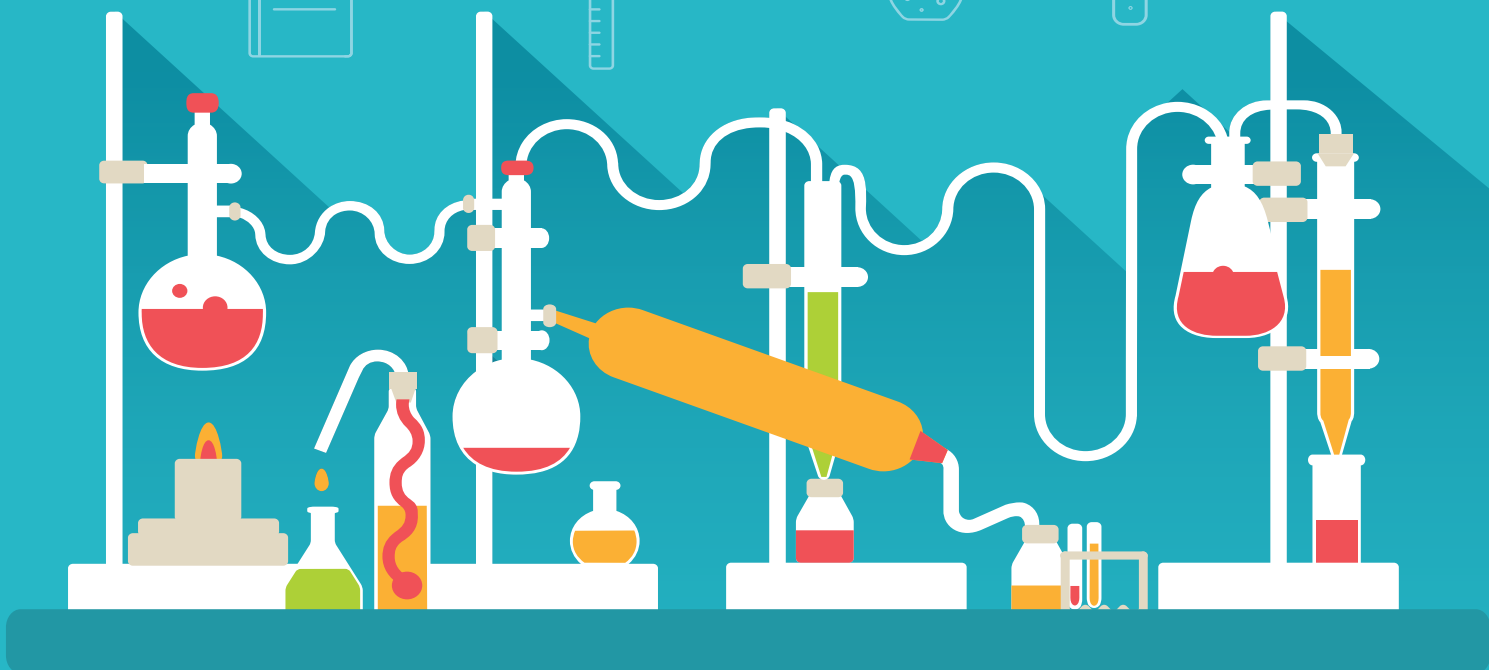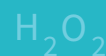# CHM220H:

Physical Chemistry for Life Sciences

Fall 2021

Week 1

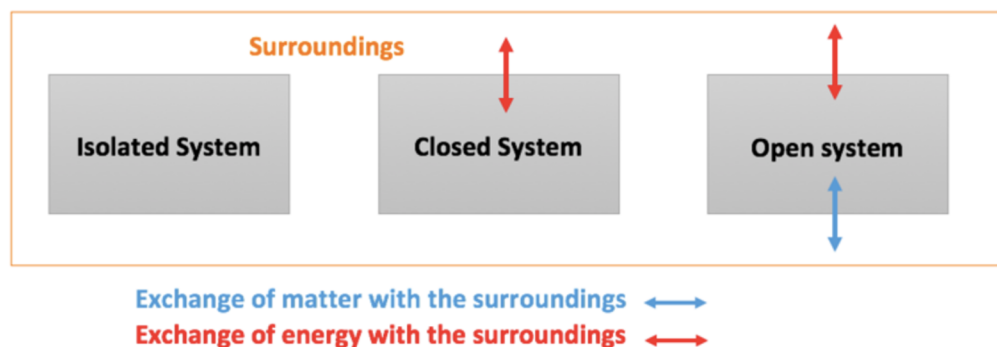## Chapter 6. First Law of Thermodynamics

知识点一：SYSTEM

1) System: all the materials involved in the process
   Surrounding: everything else

2) 三种 system:
   Open: mass and energy exchange 物质和能量都可以和外界交换
   Closed: energy exchange 只有能量可以交换 (number of particles in the system is fixed)
   Isolated: no mass nor energy exchange 什么都无法交换 (not heat transfer)

3) Variables to define a system: (they are all macroscopic variables)
   Temperature T: 温度 common units: K, °C
   Volume V: 体积 common units: L, m^3
   Pressure P: 压强 common units: bar, atm, N/m^2

4) Extensive properties: change with the amount of substance (m, V)
   Intensive properties: do not change with the amount of substance (density)

知识点一：SYSTEM

5) Thermal Equilibrium of two systems is when there is not net thermal exchange or no net macroscopic change:
   - 对于 isolated system: 不可能和另一个 system 形成 thermal equilibrium，只能自己形成 thermal equilibrium.
   - 对于 open system and closed system: (energy exchange is allowed)当与外界的温度相同时形成 thermal equilibrium.
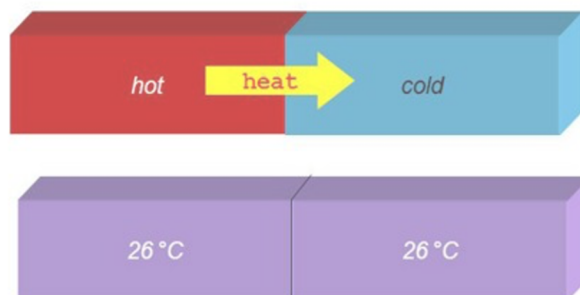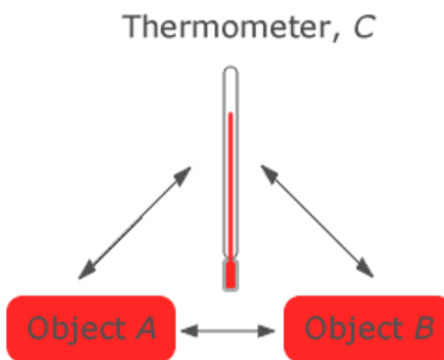

6) Zeroth law of thermodynamics:
   Two systems that are separately in thermal equilibrium with a third system are also in thermal equilibrium with one another
   A = B and B = C, then A = C
   *Then the three systems all have the same temperature

知识点二：Ideal gas law

PV = nRT

1) P: pressure in atm or Pa or N/m^2
   V: volume in L   n: moles
   R: ideal gas constant 0.08206 L atm mol^{-1}K^{-1} or 8.314 J mol^{-1}K^{-1}
   T: temperature in **Kelvin**

2) What does ideal means or the assumption of ideal gas law:
   non-interacting point particles (no attractive or repulsive forces between gas particles, and each gas particle does not occupy any volume)

3) Pressure is inversely proportional to volume: Boyle's law 压强与体积成反比
   Volume is directly proportional to temperature if P and n are kept constant: Charles' law 体积与温度成正比
   Volume is directly proportional to number of particles at constant T and P: Avogadro's law 体积与粒子个数成正比

4) At standard T and P (273 K, 1 atm): 1 mole of gas particles has a volume of **22.4 L**

5) Kelvin vs Celsius degree:
   T (K) = T (°C) + 273
   -273 °C: absolute zero, particles don't move at all

知识点三：Energy

1) Macroscopic energy:
   Kinetic energy (KE): related to the motion of an object
   Potential energy (PE): gravitational potential energy, electrical potential energy, elastic potential energy…

2) Microscopic energy: <u>Internal energy</u> (U), related to energy of molecules
   Microscopic kinetic energy: translation, vibration, rotation
   Microscopic potential energy: related to microscopic inter- and intramolecular force
   Intramolecular force: covalent bonding, ionic bonding, metallic bonding
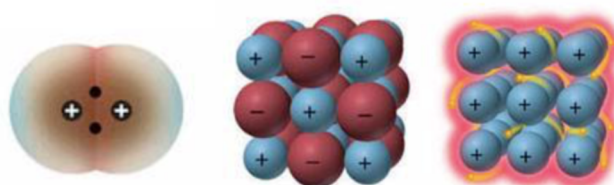
Intermolecular force: ionic interaction, dipole-dipole interaction, London force

Ion-dipole

H bond

CH_3OH

Chloroform
(CHCl$_3$)

Dipole-dipole

Octane
(C$_8$H$_{18}$)

C$_6$H$_{14}$

Dispersion
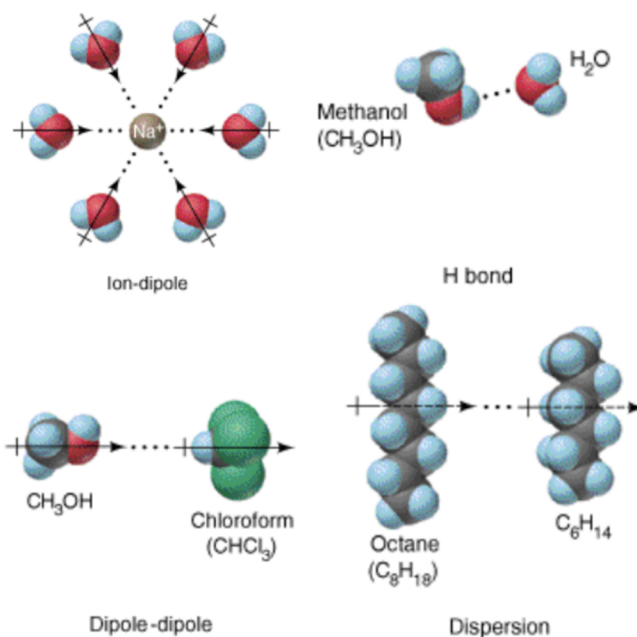
3) First Law of Thermodynamics (version #1): total energy of the universe is conserved
   Energy can neither be created nor destroyed, only be transferred.
   $dU_{total} = dU_{system} + dU_{surrounding} = 0$

知识点四：First Law of Thermodynamics

1) First Law of Thermodynamics (version #2): $\Delta U = q + w$ or **dU = dq + dw**

2) Internal energy is a **state function** (path independent). It only depends on the initial and final states.
   *remember the variables to define a state are (P, V, T)
   $(P_i, V_i, T_i) \rightarrow (P_f, V_f, T_f)$ refers to a path

3) For monoatomic ideal gas only: $U = \frac{3}{2}nRT$ U depends on T only

4) Heat (q) and work (w) are not state functions (path dependent). For different process, heat and work could be different.

5) Quasi-Static Process: all macroscopic variables undergo infinitesimal change in the process
   a) Irreversible process: $P_{ext} \neq P_{int}$
   b) Reversible process: $P_{ext} = P_{int}$
   c) Isothermal process: T is constant
   d) Adiabatic process: no heat transfer

6) Work: (取决于 external pressure and change in volume)
   work done by the surrounding on the system is positive
   work done by the system on the surround is negative

   a) $w = -P_{ext}\Delta V$ for irreversible process and constant P_{ext}
   b) $w = -\int_{vi}^{vf} P(V)dV$ for reversible process, where P is expressed as a function of V
   c) $w = -nRT\ln\frac{V2}{V1}$ for reversible isothermal process (T is constant) and for ideal gas only

Q: at constant V, $\Delta U =$?

知识点四：First Law of Thermodynamics

1) Heat: $q = m\overline{C}\Delta T = C\Delta T$

Heat transfer into the system is positive: endothermic process
Heat transfer out of the system is negative: exothermic process
Note that **C** is the heat capacity (unit: J/K)
$\overline{C}$ is the specific heat capacity, heat capacity per mol or per gram
(unit: J g^{-1}K^{-1} or J mol^{-1}K^{-1})

a) Heat Capacity: we either know the value of C (ex for water 4.184 J g^{-1}K^{-1}), or know the expression of C (ideal gas)

b) At constant volume (work = 0):
Heat Capacity $C_V = \dfrac{q}{\Delta T} = \dfrac{\Delta U}{\Delta T}$
For monoatomic ideal gas only, $\Delta U = \dfrac{3}{2}nR\Delta T$, $C_V = \dfrac{3}{2}nR$

c) At constant pressure:
Heat Capacity $C_P = \dfrac{q}{\Delta T} = \dfrac{\Delta H}{\Delta T}$

2) Enthalpy: **H = U + PV**
Enthalpy is a state function

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + P\Delta V + V\Delta P + \Delta P\Delta V$$

Thus at constant pressure $\Delta H = \Delta U + P\Delta V = q = Cp\Delta T$
For monoatomic ideal gas only: $H = \dfrac{5}{2}nRT, C_P = \dfrac{5}{2}nR$
For ideal gas, $\overline{C_P} - \overline{C_V} = R$

Summary of heat capacity for gas:

- At constant volume: q = ΔU, at constant pressure: q = ΔH
- $\Delta U = C_V \Delta T$ and $\Delta H = C_P \Delta T$
- $C_V = \frac{3}{2} nR$, $C_P = \frac{5}{2} nR$ for monoatomic idea gas.
- For non-ideal gas of which Cv and Cp are constant, you will be given with the values.
- For non-ideal system, Cp is a function of T (not a constant), then at constant pressure $q = \Delta H = \int C_P(T)\, dT$. At constant volume $q = \Delta U = \int C_v(T)\, dT$ (you will be given the expression of Cp and Cv on the test)

Summary of Equations for ideal gas only:

1) PV = nRT
2) $w = -nRT \ln\frac{V2}{V1}$ for reversible isothermal process
3) $\Delta U = \frac{3}{2} nR\Delta T$, $C_V = \frac{3}{2} nR$
4) $\Delta H = \frac{5}{2} nR\Delta T$, $C_P = \frac{5}{2} nR$
5) $\Delta U = \Delta H = 0$ for an isothermal process

1. A 7.24 g sample of ethane occupies 4.65 L at 294 K
   a) Calculate the work done when the gas expands isothermally against a constant external pressure of 0.500 atm until its volume is 6.87 L
   b) Calculate the work done if the same expansion occurs reversibly

2. An ideal gas is compressed isothermally by a force of 85 newtons acting through 0.24 meter. Calculate the values of ΔU and q.

3. An ideal gas is compressed isothermally from 2.0 atm and 2.0 L to 4.0 atm and 1.0 L. Calculate the values of $\Delta H, \Delta U$ if the process is carried out a) reversibly and b) irreversibly.

4. One mole of an ideal gas undergoes an isothermal expansion at 300k from 1.0 atm to a final pressure while performing 200 J of expansion work. Calculate the final pressure if the external pressure is 0.20 atm

5. A 10.0 g sheet of gold with a temperature of 18.0 celsius degree is laid flat on a sheet of iron that weighs 20.0 g and has a temperature of 55.6 celsius degree. Given that the specific heats of Au and Fe are 0.129 and 0.444 J g^{-1} °C^{-1}. What is the final temperature of the combined metals.

6. The constant-pressure molar heat capacity of nitrogen is given by the expression
$$\bar{C}_P = (27.0 + 5.90 \times 10^3 T - 0.34 \times 10^{-6} T^2) \, J \, K^{-1} \, mol^{-1}$$
Find the value of ΔH for heating 1 mole of nitrogen from 25.0 celsius degree to 125 celsius degree

知识点四：First Law of Thermodynamics

PV diagram:

Plot of Pressure vs Volume: the curve represents a path, the area under the curve is equivalent to <u>work</u>

1) Adiabatic process **vs** Isothermal process
2) Reversible process **vs** Irreversible process
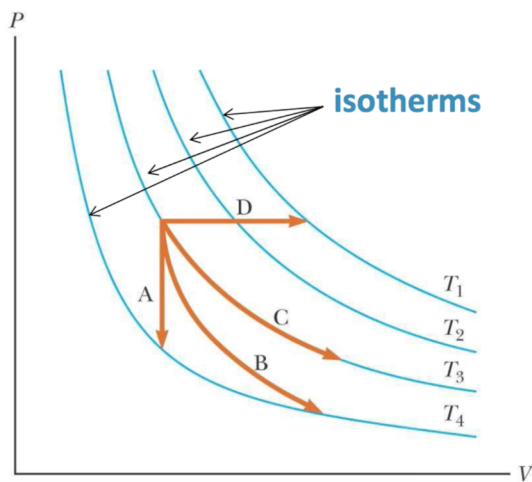
B: adiabatic (q=0)
C: isothermal (constant T), notice that C is flatter than B

1.

Four identical samples of ideal gas are initially at T_1, P_1 and V_1.

- Sample A is isothermally, reversibly compressed to V_2
- Sample B is adiabatically, irreversibly compressed to V_2
- Sample C is adiabatically, reversibly compressed to V_2
- Sample D is cooled to T_2, where $T_2 < T_1$, while also being compressed to V_2

Order the samples from lowest to highest final pressure.

2.

Four identical samples of ideal gas are initially at T_1, P_1 and V_1.

- Sample A is isothermally, irreversibly expanded to $V_2 > V_1$
- Sample B is isothermally, reversibly expanded to V_2
- Sample C is adiabatically, irreversibly expanded to V_2
- Sample D is reversibly expanded to V_2 while being heated to $T_2 > T_1$.

Order each example from lowest to highest amount of heat transferred into the system (q)

知识点五：Maxwell-Boltzmann distribution of gas particle

Maxwell-Boltzmann distribution is the probability of finding gas particles (or number of particles) with certain speed (u) or kinetic energy ($1/2mu^2$)
The probability function is related to both temperature and mass of the particle
Y-axis: number of particles, x-axis can be speed/internal energy …
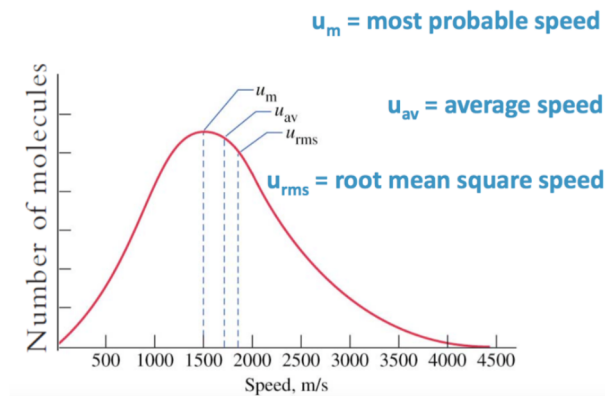
The curve looks different at different temperature
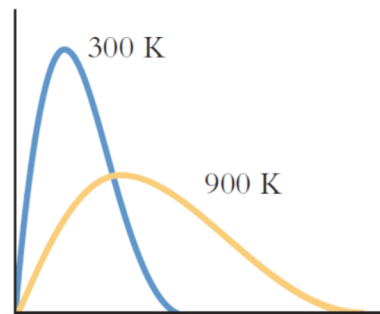
*At higher temperature: higher **probability** to find particles with higher kinetic energy

Important equation:
The population of particles with energy U_i follows the equation

$$Ni = \frac{N\,Exp\left(-\frac{Ui}{K_BT}\right)}{Q},$$

K_B = 1.4×10⁻²³J/K is called Boltzmann constant; N is the total number of particles; Q is called partition function = $\sum e^{-U/K_BT}$

*Ratio of populations of two different energy levels:

$$N_2/N_1 = e^{-\Delta U/k_BT} \text{ where } \Delta U = U_2-U_1$$