Mass transfer and separation

Lecture 3

Recap fluid mixtures, colligative properties

The kinetic theory of gases

- To be able to extract quantitative information from a qualitative model.
- Crucial for catalysis!
- According to the kinetic model a gas consists of MQs of negligible sizes in ceaseless random motion and obeying the laws of classical mechanics in their collisions.
- You need to be aware of Newton's 2nd law of motion, i.e. $a=F/m$
- Assumption: the only contribution to the energy of a gas is the kinetic energy of MQs.

Objectives

- Describe the motion of all types of particles in all types of fluids
- Concentrate of transportation properties:
  - Diffusion ≡ migration of matter down a concentration gradient
  - Thermal conduction ≡ migration of energy down a temperature gradient
  - Electrical conduction ≡ migration of charge along a potential gradient
  - Viscosity ≡ migration of linear momentum down a velocity gradient

Kinetic Molecular Theory (KMT) of Gases

- A gas is composed of widely-separated MQs.
  - MQs can be considered to be points; that is, they possess mass but have negligible volume.
- Gas MQs are in constant random motion.
- Collisions among MQs are perfectly elastic.
  - Elastic collision: when the total translational kinetic energy is conserved.
- The average kinetic energy of MQs is proportional to the temperature of the gas in Kelvins.

$$\text{KE} \propto T$$

Pressure of gas according to the kinetic model

- When a particle of mass m is travelling with a component of velocity of v_x parallel to the x-axis collides with the wall and is reflected, its linear momentum changes from mv_x to $-mv_x$.
- The x-component of momentum changes by $2mv_x$ on each collision (while y and z are unchanged).
- Many MQs collide with the wall in a Δt interval; the total momentum change, $\Delta p_{total} = \Delta p_i N$, N=# of MQs that reach the wall in Δt.
- As a MQ with v_x may travel $v_x\Delta t$ distance, all MQs $v_x\Delta t$ away from the wall will strike it.
- If the wall has an area of A, MQs in the $Av_x\Delta t$ volume will reach the wall.
- With number density of MQs of nN_A/V, the # of MQs in this volume is $(nN_A/V)Av_x\Delta t$.

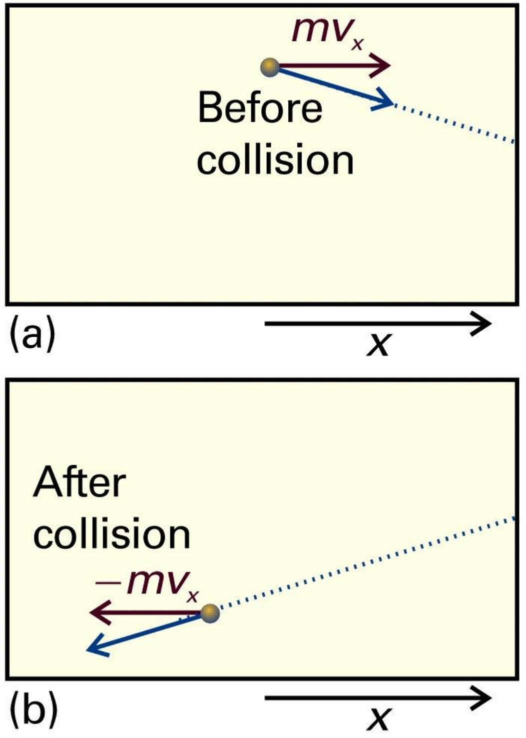
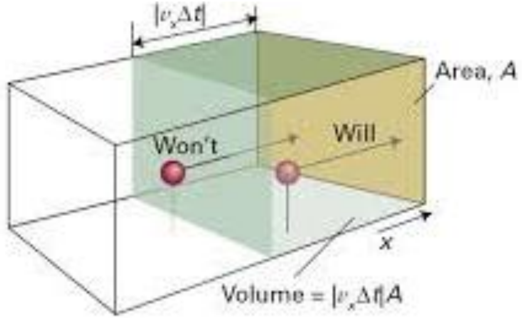


Figure 21-1
Atkins Physical Chemistry, Eighth Edition
© 2006 Peter Atkins and Julio de Paula

Pressure of gas according to the kinetic model

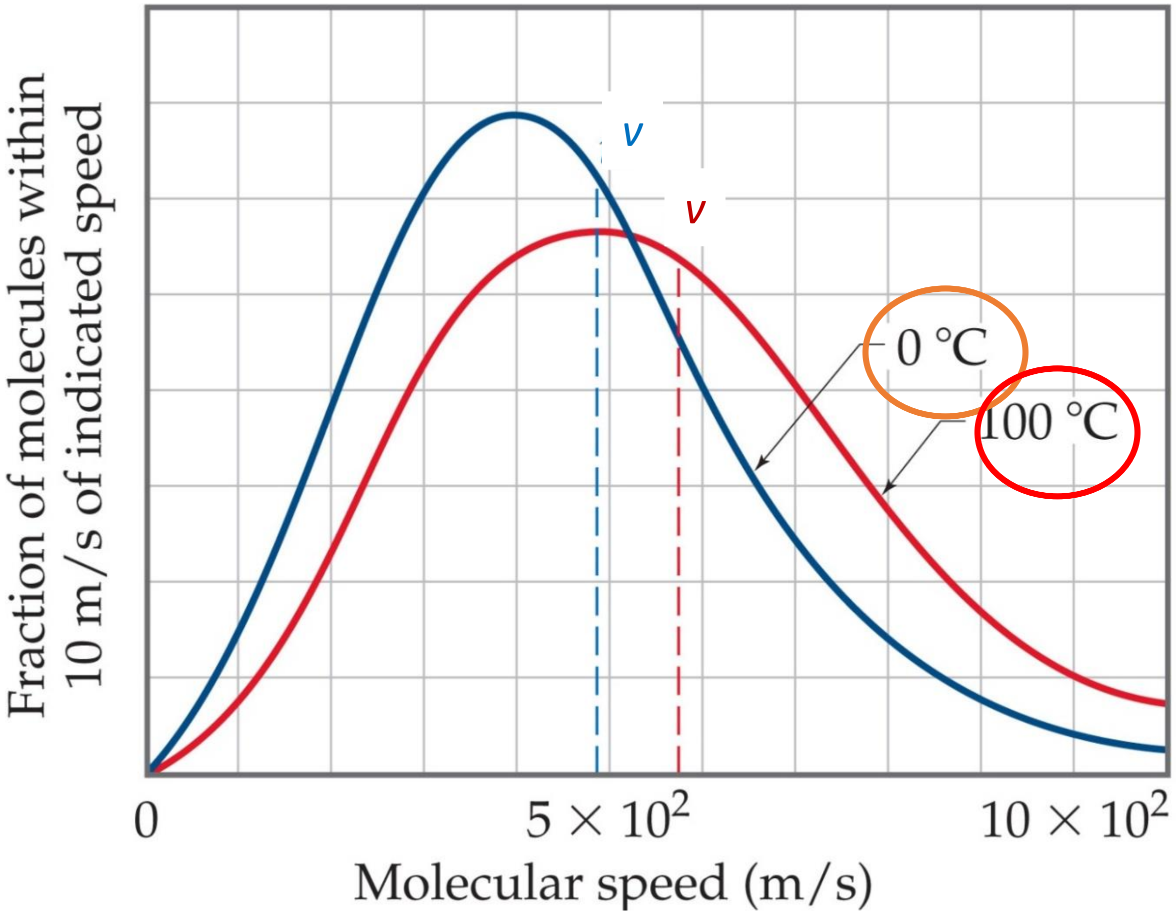


- At any instant ½ of MQs are moving towards the wall, another ½ away from it. Therefore, the average # of collisions with the wall $1/2nN_A Av_x\Delta t/V$.
- $\Delta p_{tot} = \frac{nN_A Av_x\Delta t}{2V} \times 2mv_x = \frac{nmN_A Av_x^2\Delta t}{V} = \frac{nMAv_x^2\Delta t}{V}$
- To find the force, we calculate $\frac{\Delta p_{tot}}{\Delta t} = \frac{nMAv_x^2}{V}$, the rate of momentum change
- Newton's 2nd law: rate=F
- pressure: p=F/A $= \frac{nMv_x^2}{V}$; and as not all MQs travel with the same velocity, the average (*i.e.* detected) pressure $p = \frac{nM<v_x^2>}{V}$, similar to the perfect gas equation of state.

Pressure and MQlar speeds

- For a single MQ: $v^2 = v_x^2 + v_y^2 + v_z^2$ and as $v_{RMS} = \langle v^2 \rangle^{1/2}$ so $v_{RMS}^2 = v^2 = v_x^2 + v_y^2 + v_z^2$.
- As the MQs move randomly $v_x^2 = v_y^2 = v_z^2$ on average and so $v_{RMS}^2 = 3\langle v_x^2 \rangle$ and $\langle v_x^2 \rangle = \frac{1}{3} v_{RMS}^2$
- $p = nM\langle v_x^2 \rangle / V$, sub eq. $pV = \frac{1}{3} nMv_{RMS}^2$, for a perfect gas, where $M = mN_A$.
- The v_{RMS} of MQs depends only on T as pV=constant (Boyle's law). For it to be an equation of state: $pV=nRT$.
- The RMS speed of MQs: $v_{RMS} = \left(\frac{3RT}{M}\right)^{1/2}$ for a perfect gas.

Effect of *T* on MQlar speeds

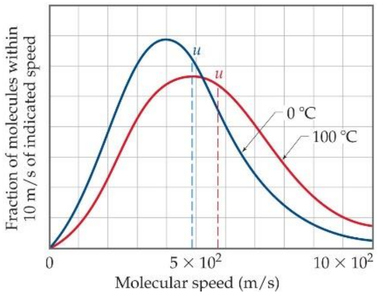


$$v_{RMS} = \left(\frac{3RT}{M}\right)^{1/2}$$

R = 8.314 J/(mol K)

Hot molecules are *fast*, cold molecules are *slow.*

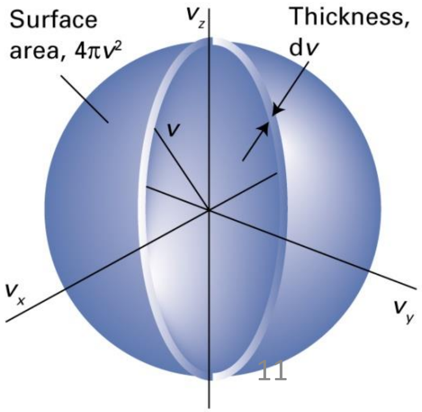
Maxwell-Boltzmann distribution of speeds



- Boltzmann distribution $f(v)=Ke^{-\varepsilon/kT} \rightarrow$ fraction of MQs with velocity components of v_x, v_y and v_z is proportional to an exp. function of their kinetic energy
- $\varepsilon = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2$, kinetic energy → $f(v) = Ke^{-(mv_x^2+mv_y^2+mv_z^2)/2kT} = Ke^{-mv_x^2/2kT}e^{-mv_y^2/2kT}e^{-mv_z^2/2kT}$.
- The distribution factorises into $f(v_x) = K_x e^{-mv_x^2/2kT}$, *etc.*
- To determine the K_x constant, recognise that a MQ must have a velocity component in the range of $-\infty<v_x<\infty$, so $\int_{-\infty}^{\infty} f(v_x)\,\mathrm{d}v_x = 1$.
- This is a Gaussian function ($\int_0^{\infty} e^{-ax^2}\,\mathrm{d}x = \frac{1}{2}\left(\frac{\pi}{a}\right)^{\frac{1}{2}}$), so $1 = K_x \int_{-\infty}^{\infty} e^{-mv_x^2/2kT}\,\mathrm{d}v_x = K_x\left(\frac{2\pi kT}{m}\right)^{\frac{1}{2}}$.
- Therefore, $K_x = (m/2\pi kT)^{1/2}$ so $f(v_x) = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_x^2/2kT}$

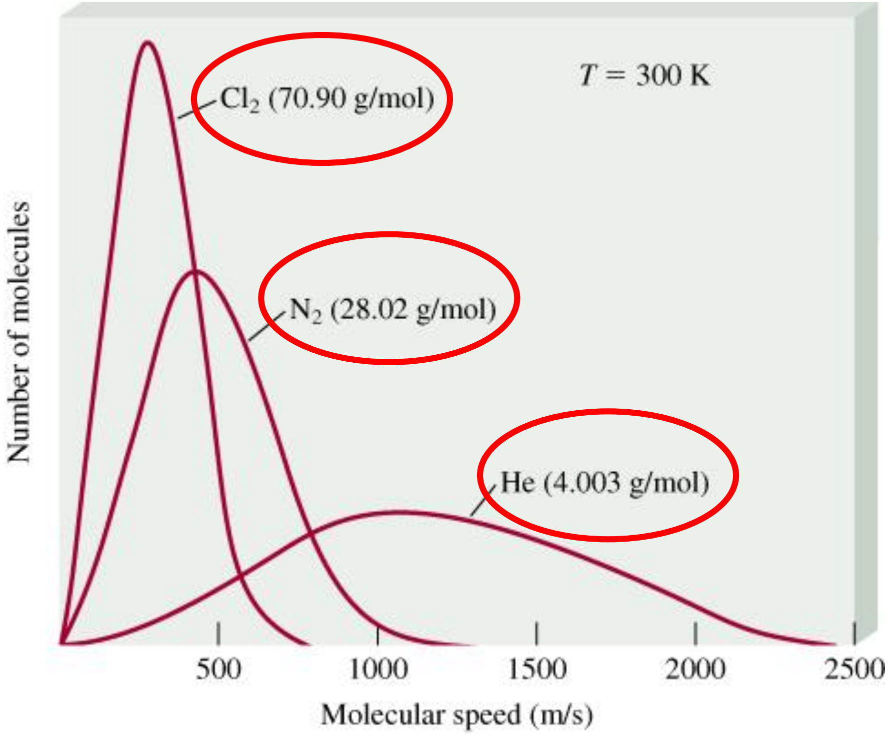
Maxwell-Boltzmann distribution of speeds

- The probability of a MQ having a velocity in the range of v_x to v_x+dv_x, v_y to v_y+dv_y, and v_z to v_z+dv_z is: $f(v_x)f(v_y)f(v_z)\mathrm{d}v_x\mathrm{d}v_y\mathrm{d}v_z = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mv_x^2/2kT}e^{-mv_y^2/2kT}e^{-mv_z^2/2kT}\mathrm{d}v_x\mathrm{d}v_y\mathrm{d}v_z = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mv^2/2kT}\mathrm{d}v_x\mathrm{d}v_y\mathrm{d}v_z$, since $v^2=v_x^2+v_y^2+v_z^2$
- To evaluate the probability of a MQ having speed off v to v+dv regardless of the direction, we consider the shell of the velocity space: $f(v)\mathrm{d}v = 4\pi v^2\mathrm{d}v\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mv^2/2kT}$
- $f(v) = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-mv^2/2kT}$.



Effect of Molecular Mass on MQlar Speeds

- The distribution of speeds of three different gases at the same temperature



$$v_{RMS} = \left(\frac{3RT}{M}\right)^{1/2}$$

Heavy molecules are *slow*, **light molecules** are *fast*

Features of the Maxwell –Boltzmann distribution of speeds

- Maxwell distribution for fraction (*f*) of molecules with speeds from *v* to *v*+d*v*

$$f(v) = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-mv^2/2kT}$$

$$f(v) = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} v^2 e^{-Mv^2/2RT}$$

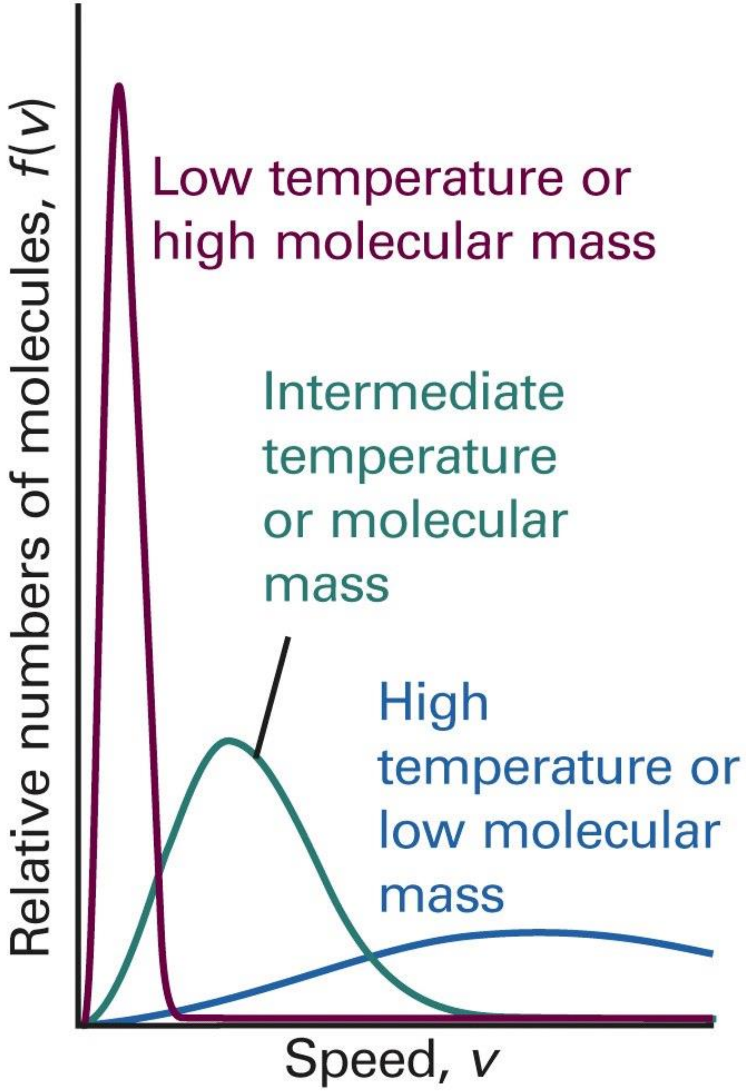


Figure 21-3
Atkins Physical Chemistry, Eighth Edition

Maxwell-Boltzmann distribution of speeds

- The $f(v) = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} v^2 e^{-Mv^2/2RT}$ function is called Maxwell-Boltzmann distribution of speeds, we use the distribution to calculate the average value of v^2.
- Decaying exponential – very few high speed molecules
- M/2RT forces exp to zero for high molar mass molecules
- M/2RT keeps exp high for high temperatures
- v^2 exp → 0 as v → 0: few slow molecules
- Remaining factors ensure that all speeds are normalised

Obtaining probability

$$f(v) = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} v^2 e^{-Mv^2/2RT}$$

- The Maxwell-Boltzmann distribution can be used to evaluate the fraction of MQs in the range of v_1 to v_2
- to obtain this we integrate $f(v)$ between v_1 and v_2 $\mathrm{F}(v_1, v_2) = \int_{v_1}^{v_2} f(v)\mathrm{d}v$

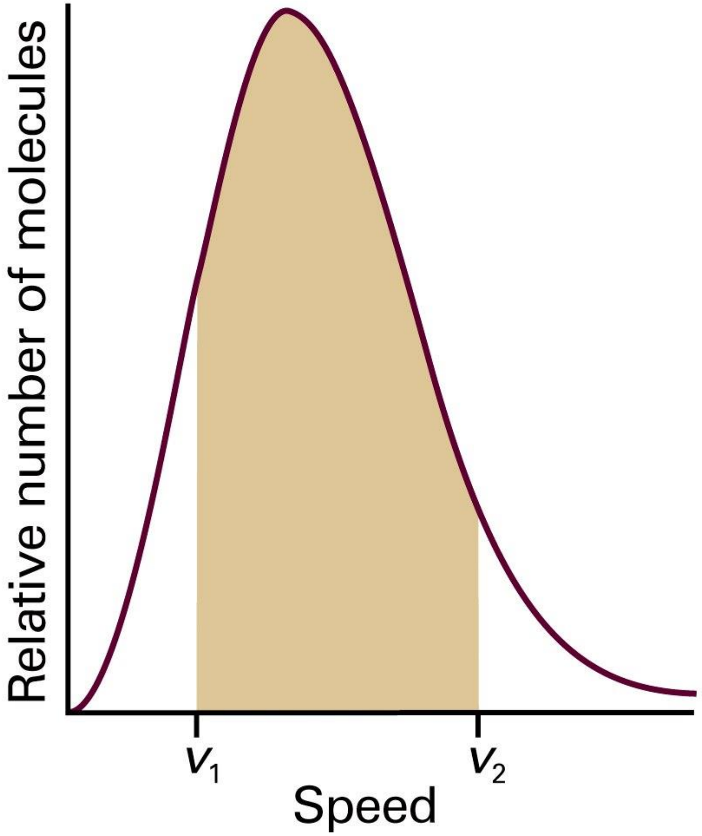


Figure 21-4
Atkins Physical Chemistry, Eighth Edition

Velocity selector

- The Maxwell-Boltzmann distribution has been verified experimentally, MQlar speeds can be measured directly with a velocity selector.
- The spinning cylinder has channels that permit the passage of only those MQs with appropriate speed, their # is determined by collection at detector.

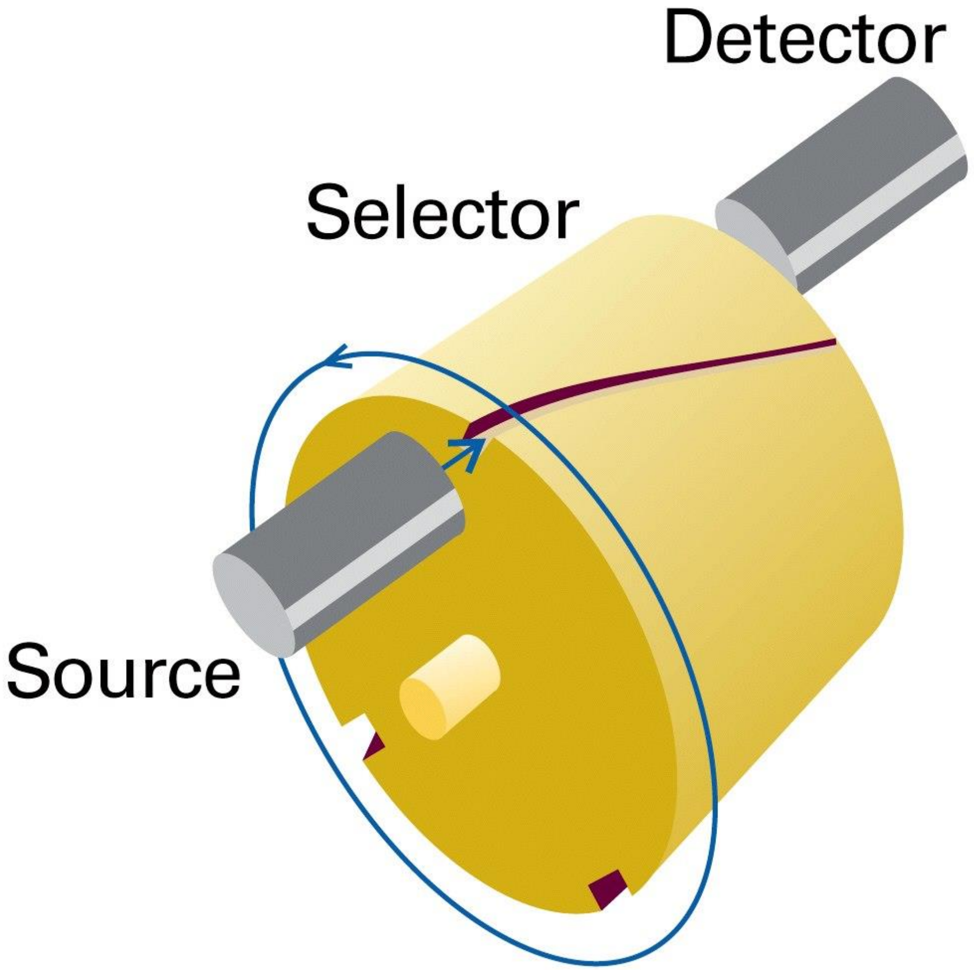


Figure 21-8
Atkins Physical Chemistry, Eighth Edition
© 2006 Peter Atkins and Julio de Paula

Mean values

$$f(v) = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} v^2 e^{-Mv^2/2RT}$$

- Once we have the Maxwell-Boltzmann distribution we can calculate the mean value of any power of the speed by evaluating the appropriate integral: $\langle v^n \rangle = \int_0^\infty v^n f(v)\mathrm{d}v$.
- Integration with *n*=2 results in $v_{RMS} = \left(\frac{3RT}{M}\right)^{1/2}$.
- v_{RMS} α $T^{1/2}$ and v_{RMS} α $1/M^{1/2}$
- → T↑ v_{RMS} ↑ and M↑ v_{RMS}↓

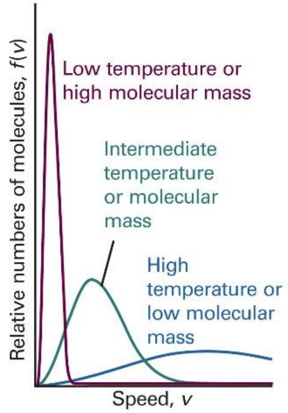


Figure 21-3
Atkins Physical Chemistry, Eighth Edition
© 2006 Peter Atkins and Julio de Paula

- Sound waves are pressure waves and for them to propagate MQs of the gas must move to form regions of high & low pressures.
- → v_{RMS} of MQs should be comparable with the speed of sound (340 m s^{-1})

Mean speed of MQs in a gas

- Calculate the speed, v_{mean}, of N_2 (M=28.02 g mol^{-1}) MQs at 25 °C.
- Use $v_{mean} = \int_0^\infty v f(v) \mathrm{d}v$
- Reminder: $f(v) = 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} v^2 e^{-Mv^2/2RT}$
- Remember that $\int_0^\infty x^3 e^{-ax^2} \mathrm{d}x = \frac{1}{2a^2}$ (common integrals)

Answer

$$\int_0^{\infty} x^3 e^{-ax^2} \mathrm{d}x = \frac{1}{2a^2}$$

- $v_{mean} = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} \int_0^{\infty} v^3 e^{-Mv^2/2RT}\,\mathrm{d}v$
- $v_{mean} = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} \frac{1}{2}\left(\frac{2RT}{M}\right)^{1/2} = \left(\frac{8RT}{\pi M}\right)^{1/2}$ =475 m s^{-1}

Conclusion of the Maxwell-Boltzmann distribution

- Mean speed: $v_{mean} = \left(\frac{8RT}{\pi M}\right)^{1/2}$, for a perfect gas
- Most probable speed: $v_{mp} = \left(\frac{2RT}{\pi M}\right)^{1/2}$
- Relative mean speed: $v_{rel} = 2^{1/2} v_{mean}$, perfect gas, identical MQs
- Relative speed of 2 dissimilar MQs of masses m_A and m_B: $v_{rel} = \left(\frac{8kT}{\pi\mu}\right)^{1/2}$, where $\mu = \frac{m_A m_B}{m_A+m_B}$

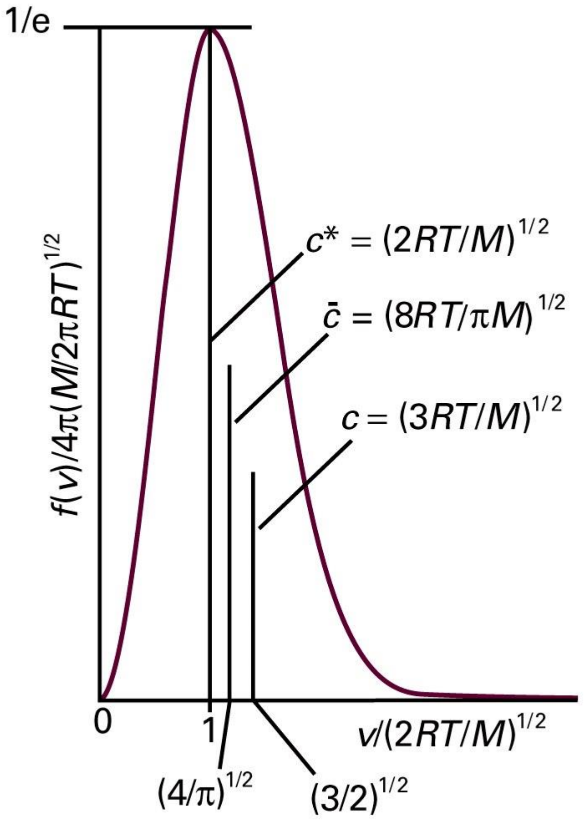
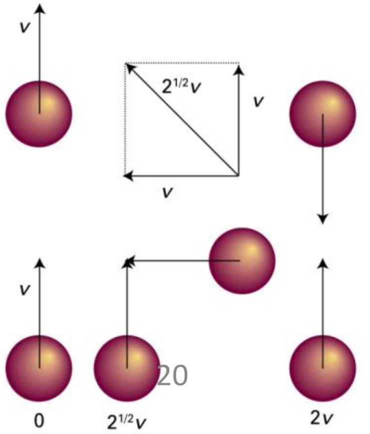


Figure 21-6
Atkins Physical Chemistry, Eighth Edition
© 2006 Peter Atkins and Julio de Paula



MQlar collisions

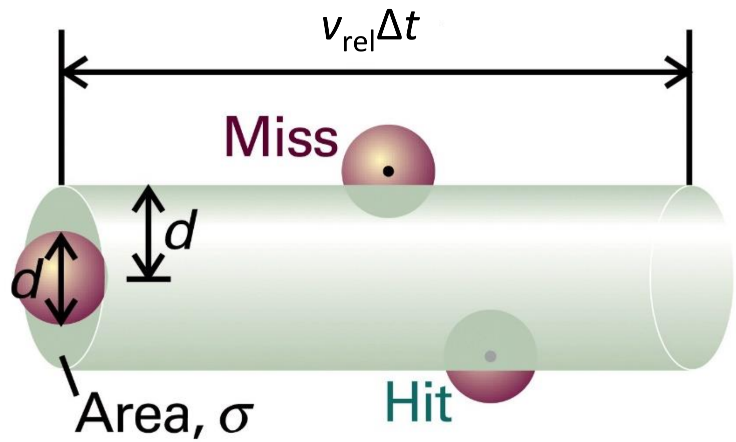


Figure 21-9
Atkins Physical Chemistry, Eighth Edition
© 2006 Peter Atkins and Julio de Paula

- Although the kinetic-MQlar theory assumes that MQs are point-like, we can count a ‘hit’ whenever the MQs’ centres come within a *d* distance from each other.
- *d* is called the collision diameter, it is in the order of the actual diameter of MQs.
- Consider MQs except 1 ‘frozen’, when the mobile MQ travels through the gas with v_{rel} (relative speed) during Δt, it sweeps out a collision tube of cross section area $\sigma=\pi d^2$ and length $v_{rel}\Delta t$, *i.e.* of volume $\sigma v_{rel}\Delta t$.
- # of stationary MQs with centres inside the tube is given by the volume of the tube multiplied by the number density ($\mathcal{N}=N/V$) as $\mathcal{N}\sigma v_{rel}\Delta t$.
- In terms of pressure this yields: $\mathcal{N}=\frac{N}{V}=\frac{nN_A}{V}=\frac{nN_A}{nRT/p}=\frac{p}{kT}$

Collision frequency

- The collision frequency for a perfect gas is given as the number of hits as a function of time, i.e. $\mathcal{N}\sigma v_{\mathrm{rel}}\Delta t/\Delta t$: $z = \sigma v_{rel}\mathcal{N}$
- At constant volume, z↑ with T↑
- In terms of pressure (we have seen that $\mathcal{N} = \frac{p}{kT}$): $z = \frac{\sigma v_{rel} p}{kT}$
- At constant temperature $z \propto p$ (number density ↑ when p↑)
- The area $\sigma = \pi d^2$ is called the collision cross-section of the MQs.

Molecular collisions

- For a N_2 MQ at 101 kPa and 25 °C v_{mean}=475 m s^{-1}.
- Using σ=0.43 nm^2, determine the collision frequency.

- Note that $v_{\text{rel}}=2^{1/2}v_{\text{mean}}$
- Use $z = \frac{\sigma v_{rel} p}{kT}$

Answer

- $z = \frac{\sigma v_{rel} p}{kT} = \frac{(0.43*10^{-18} m^2)(2^{\frac{1}{2}}*475\ m\ s^{-1})(1.01*10^5\ Pa)}{(1.381*10^{-23} J\ K^{-1})(298\ K)} = 7.1 * 10^9\ s^{-1}$
- So a given MQ collides *ca.* 7*10^9 times every second!

Mean free path

- From *z* we may calculate the mean free path: $\lambda = \frac{v_{rel}}{z}$, for a perfect gas, with a pressure dependence of $\lambda = \frac{kT}{\sigma p}$.
- Doubling the pressure decreases mean free path by half.
- Although *T* appears in eq. in a sample of constant *V*: *p* α *T* so *T*/*p* remains constant. Therefore, the mean free path is independent of *T* in a sample of gas in a contained of fixed *V*.
- Typically $\lambda \approx$ 70 nm for nitrogen at 1 atm
- $v \approx 500$ m s^{-1} at 298 K

Mean free path

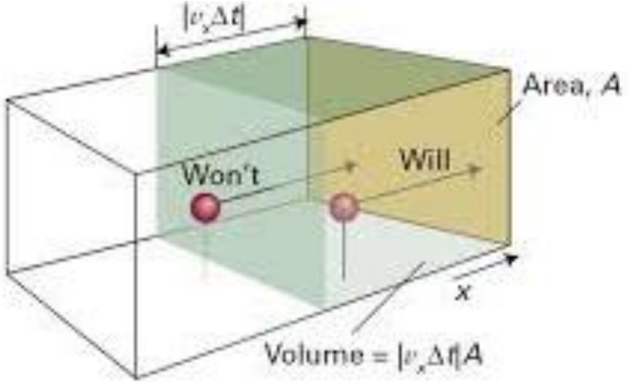
- What is the mean free path for N_2 MQs if v_{mean}=475 m s^{-1} at 25 °C, and if z=7.1*10^9 s^{-1} at 1.00 atm.

- $v_{rel}=2^{1/2}v_{mean}$
- $\lambda = \frac{v_{rel}}{z}$

Answer

- $\lambda = \frac{v_{rel}}{z} = \frac{2^{1/2} v_{mean}}{z} = \frac{2^{1/2} * 475\ m\ s^{-1}}{7.1 * 10^{9} s^{-1}} = 9.5 * 10^{-8} m.$

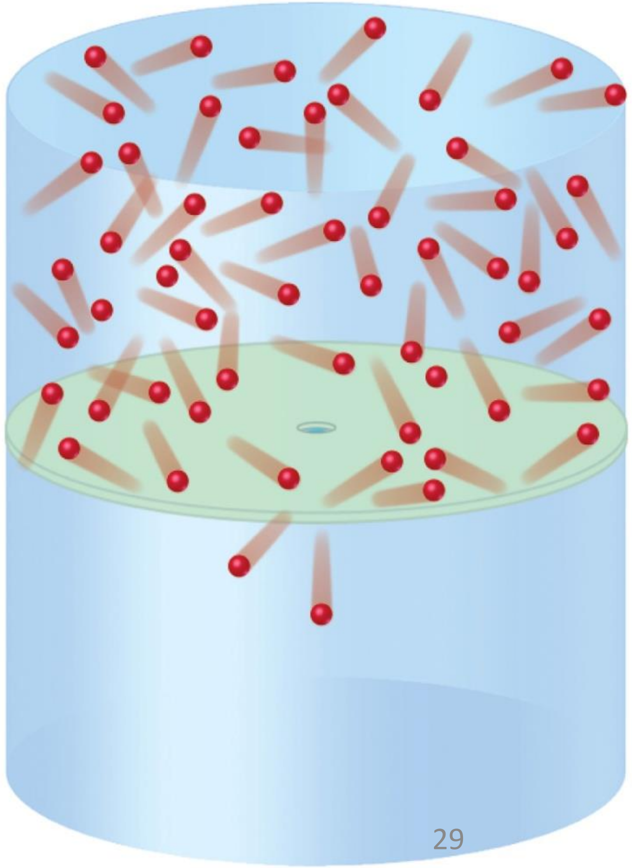
Collisions with walls and surfaces



- Key result for accounting for transport in the gas phase is the rate at which MQs strike an area.
- Consider a wall of area *A*, perpendicular to the *x*-axis.
- If a MQ has $v_x>0$, it will strike the wall within Δt if it lies within a distance of $v_x\Delta t$ from the wall.
- All MQs in the $Av_x\Delta t$ volume and with a +ve *x* component will strike it.
- The total # of collisions is $\mathcal{N}Av_x\Delta t$. However, to take account of a range of velocities we must integrate: # collisions= $\mathcal{N}A\Delta t\int_0^\infty v_x f(v_x)\,\mathrm{d}v_x$.
- The collision flux is the # of collisions divided by the area and time interval: $Z_W = \mathcal{N}\int_0^\infty v_x f(v_x)\,\mathrm{d}v_x$, and as $\int_0^\infty v_x f(v_x)\,\mathrm{d}v_x = \left(\frac{m}{2\pi kT}\right)^{1/2}\int_0^\infty v_x\, e^{-mv_x^2/2kT}\mathrm{d}v_x = \left(\frac{kT}{2\pi m}\right)^{1/2}$ (Consider: $\int_0^\infty xe^{-ax^2}\,\mathrm{d}x = \frac{1}{2a}$, common integrals)
- $Z_W = \mathcal{N}\left(\frac{kT}{2\pi m}\right)^{1/2}$, then substitute $\mathcal{N}=p/kT$.
- The collision flux: $Z_W = \frac{p}{(2\pi mkT)^{1/2}}$, for a perfect gas.

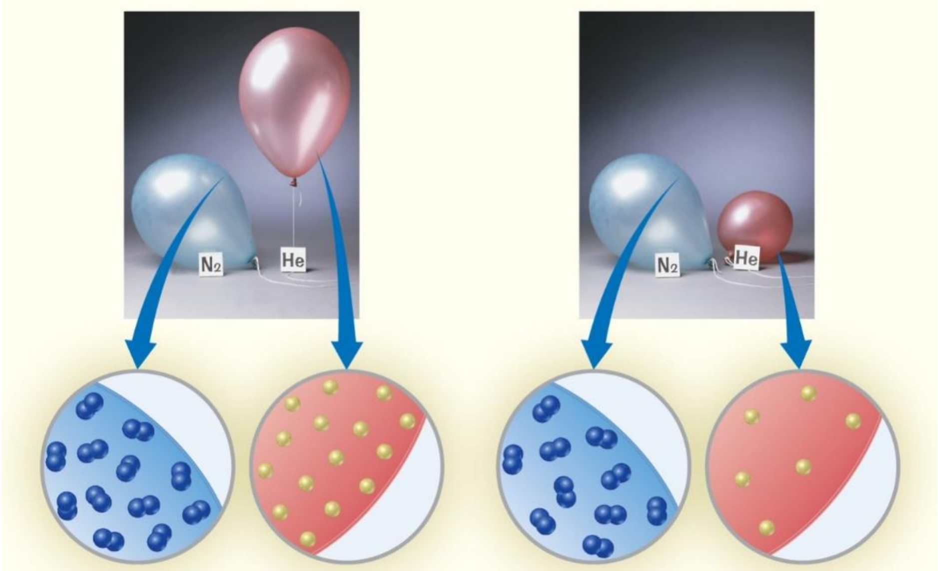
Effusion

- !a gas with p & T separated from vacuum by a small hole; the rate of escape of MQs equals the rate at which they strike the hole.
- For the A_0 area: Rate of effusion$= Z_W A_0 = \frac{pA_0}{(2\pi mkT)^{1/2}}$.
- As $M=mN_A$, this is inversely proportional to $M^{1/2}$.



Effusion

- Empirical observations summarised by Graham's law of effusion, stating that the rate of effusion α $1/M^{1/2}$.
- As we've seen $v_{mean} = \left(\frac{8RT}{\pi M}\right)^{1/2}$, so will be the rate through which MQs strike a hole.



Two balloons are filled to the same volume, one with nitrogen and one with helium.

After 48 hours, the helium-filled balloon is smaller than the nitrogen-filled one because helium escapes faster than nitrogen.

Calculating vapour pressure from mass loss

- Caesium (m.p. 29 °C, b.p. 686 °C) was introduced into a container and heated at 500 K. When a hole of diameter 0.50 mm was opened in the container for 100 s, a mass loss of 385 mg was measured.
- Calculate the vapour pressure of liquid caesium at 500 K. Note, this is called the *Knudsen method*.
- Use $\Delta m = Z_W A_0 m \Delta t$ (Z_W – collision flux $Z_W = \frac{p}{(2\pi m k T)^{1/2}}$)

Answer

- p_{vap} is constant inside the container despite the hole as the hot liquid replenished the vapour phase. The rate of effusion is therefore also constant.
- $\Delta m = Z_W A_0 m \Delta t = \frac{p A_0 m \Delta t}{(2\pi m k T)^{1/2}} = \frac{p A_0 m^{1/2} \Delta t}{(2\pi k T)^{1/2}}.$
- $p = \left(\frac{2\pi k T}{m}\right)^{1/2} \frac{\Delta m}{A_0 \Delta t} = \left(\frac{2\pi R T}{M}\right)^{1/2} \frac{\Delta m}{A_0 \Delta t}$=8.7*10^{3} kgm^{-1}s^{-2} (Pa)

Transport properties of gases

- Plays an important role in the atmosphere; kinetic theory extended to extract quantitative expressions
- A MQ carries properties through space for the distance of its mean free path.
- Describe the motion of all types of particles in all types of fluids

Phenomenological equations

- Transport properties are commonly expressed in terms of 'phenomenological equations'.
- They are empirical summaries of experimental observations, without (initially) being based on the understanding of MQlar processes responsible for the property.
- Net rate of transport of a property is measured by its flux, *J*, the quantity of that property passing through a given area in a given time interval (property/(area*duration)).
- If matter is flowing (*cf.* diffusion) → matter flux (#MQs/m^2s), if it's energy (*cf.* thermal conduction) → energy flux (J/m^2s).

Fick's 1st law of diffusion

- Experiments show that J α 1st derivative of some other related property.
  - $J(matter) \propto \frac{d\mathcal{N}}{dz}$,$\mathcal{N}$- # density of particles per unit V.
- Proportionality of J(matter) to concentration is given by Fick's first law of diffusion;
  - If the concentration gradient varies steeply with position, then diffusion will be fast.
- There is no net flux is the concentration is uniform
- Similarly rate of thermal conduction α temperature gradient; $J(energy\ of\ thermal\ motion) \propto \frac{dT}{dz}$.

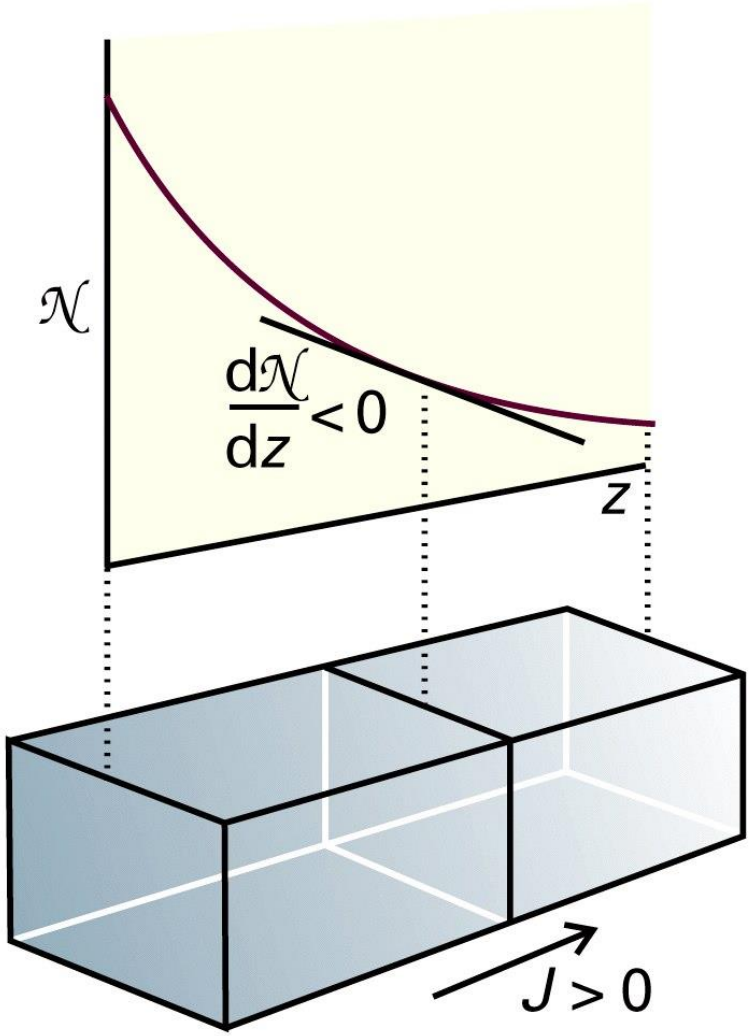


Figure 21-10
Atkins Physical Chemistry, Eighth Edition

Phenomenological parameters: mass and heat

- +ve *J* : flux towards +ve *z* and vice versa.
- As matter flows from high concentration towards low, *J* is +ve when $\frac{d\mathcal{N}}{dz}$ is –ve, thus the coefficient of proportionality must be –ve.
- Diffusion coefficient; $J(matter) = -D\frac{d\mathcal{N}}{dz}$. [D]=$m^2s^{-1}$
- Similarly, energy of thermal motion (heat) migrates high *T* towards low; $J(energy\ of\ thermal\ motion) = -\kappa\frac{dT}{dz}$, thermal conductivity [$JK^{-1}m^{-1}$ or $WK^{-1}m^{-1}$]

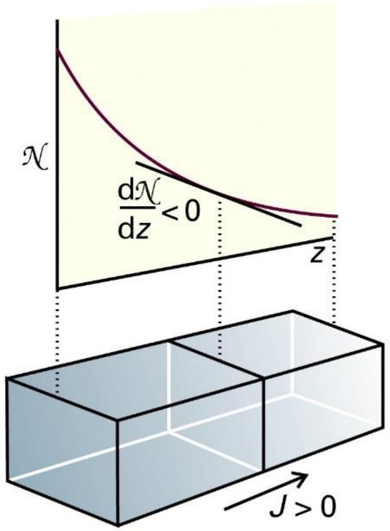


Figure 21-10
Atkins Physical Chemistry, Eighth Edition
© 2006 Peter Atkins and Julio de Paula

Phenomenological parameters: momentum

- To see connection btw *J*(momentum) & viscosity – consider a Newtonian (laminar) flow; a series of layers moving past each other
- The layer next to the wall – stationary, velocity of successive layers varies linearly w distance, *z*.
  - If the entering layer has high linear momentum, it accelerates the layer
  - If the entering layer has low linear momentum, it retards the layer
- As retarding effect depends on transfer of the *x*-component of linear momentum into the layer of interest, the viscosity depends on the flux of *x*-component in the *z*-direction
  - flux of *x*-component α dv_x/dz as there is no net flux when all layers move w the same *v*.
- Viscosity: $J(x - component\ of\ momentum) = -\eta \frac{dv_x}{dz}$; [kgm^{-1}s^{-1}, or Pa s]

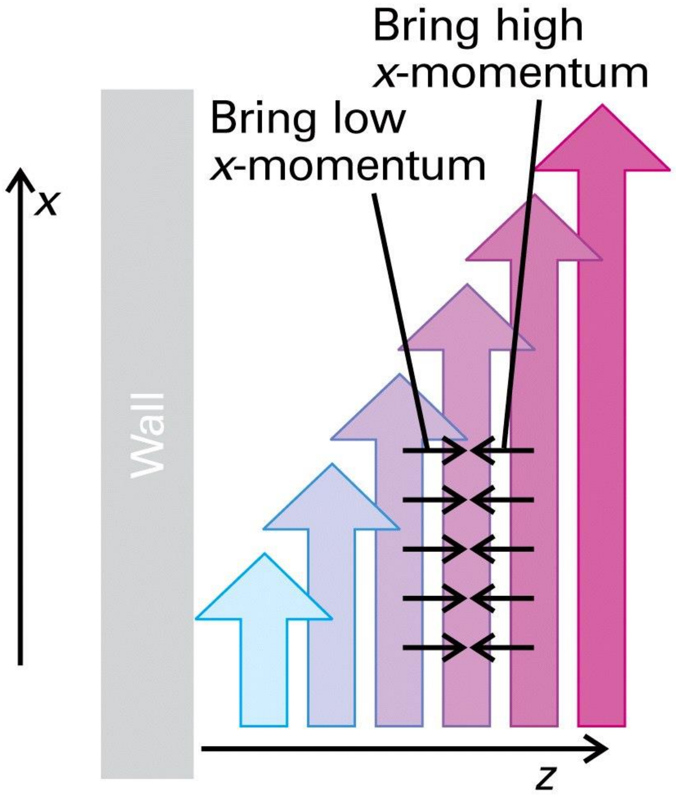
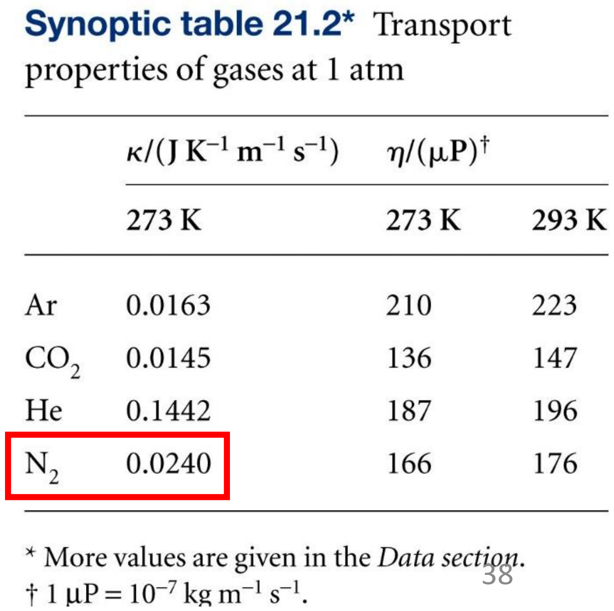


Figure 21-11
Atkins Physical Chemistry, Eighth Edition
© 2006 Peter Atkins and Julio de Paula

Energy flux

- Suppose a T difference of 10 K between 2 metal plates separated by 1.0 cm.
- What is the energy flux for κ=0.024 J K^{-1} m^{-1}?
- How much energy would be transferred between the two plates in 1h?

- $J(energy\ of\ thermal\ motion) = -\kappa \frac{dT}{dz}$



Synoptic table 21.2* Transport properties of gases at 1 atm

	$\kappa/(\mathrm{J\ K^{-1}\ m^{-1}\ s^{-1}})$	$\eta/(\mu\mathrm{P})^{\dagger}$	
	273 K	273 K	293 K
Ar	0.0163	210	223
CO_2	0.0145	136	147
He	0.1442	187	196
N_2	0.0240	166	176

* More values are given in the *Data section*.
† 1 μP = 10^{-7} kg m^{-1} s^{-1}.

Answer

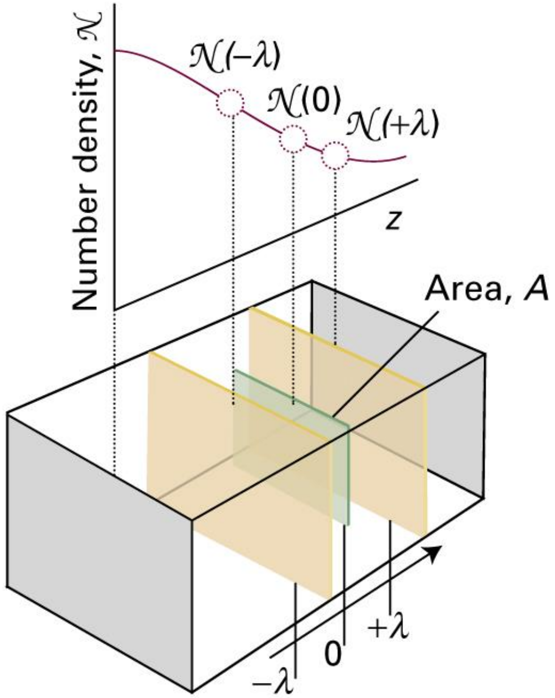
- The temperature gradient is dT/dz=- 10K/(1.0*10^{-2} m)=-1.0*10^{3} K m^{-1}
- The energy flux in air is:

J(energy of thermal motion)=-(0.024 J K^{-1} m^{-1} s^{-1})*(-1.0*10^{3} K m^{-1})=

+24 J m^{-2} s^{-1}

- As a result, in 1.0 h (3600 s) the transfer of energy through an area of the opposite walls of 1.0 cm^{2} is:
- Transfer=(24 J m^{-2} s^{-1})*(1.01*10^{-4} m^{2})*(3600 s)=8.6 J

Transport parameters



- On average, MQs passing through *A* area at *z*=0 have travelled *ca.* λ (mean free path) since their last collision.
- $\mathcal{N}(z)$ – evaluated at $z=-\lambda$; using Taylor expansion truncated after 2nd term;
- $\mathcal{N}(-\lambda) = \mathcal{N}(0) - \lambda\left(\frac{d\mathcal{N}}{dz}\right)_0$ and $\mathcal{N}(\lambda) = \mathcal{N}(0) + \lambda\left(\frac{d\mathcal{N}}{dz}\right)_0$
- Average # of impact on the imaginary window of A_0 during Δt interval is $Z_W A_0 \Delta t$.
- Z_W – collision flux, or $Z_W = \mathcal{N}\left(\frac{kT}{2\pi m}\right)^{1/2} = \frac{1}{4}\mathcal{N}v_{mean}$.
- So the left to right flux: $J(L \rightarrow R) = \frac{\frac{1}{4}\mathcal{N}(-\lambda)v_{mean}A_0\Delta t}{A_0\Delta t} = \frac{1}{4}\mathcal{N}(-\lambda)v_{mean}$
- From right to left: $J(L \leftarrow R) = \frac{1}{4}\mathcal{N}(\lambda)v_{mean}$

Diffusion coefficient

- The net flux from left to right therefore is: $J_z = J(L \rightarrow R) - J(L \leftarrow R) = \frac{1}{4} v_{mean}\{\mathcal{N}(-\lambda) - \mathcal{N}(\lambda)\} = \frac{1}{4} v_{mean}\left\{\left[\mathcal{N}(0) - \lambda\left(\frac{d\mathcal{N}}{dz}\right)_0\right] -\right.$

Diffusion coefficient

- $\lambda(N_2)$=95 nm at 1.0 bar, their v_{mean}=475 ms^{-1} at 25 °C.
- What is their diffusion coefficient?

- $D = \frac{1}{3}\lambda\, v_{mean}$

Answer

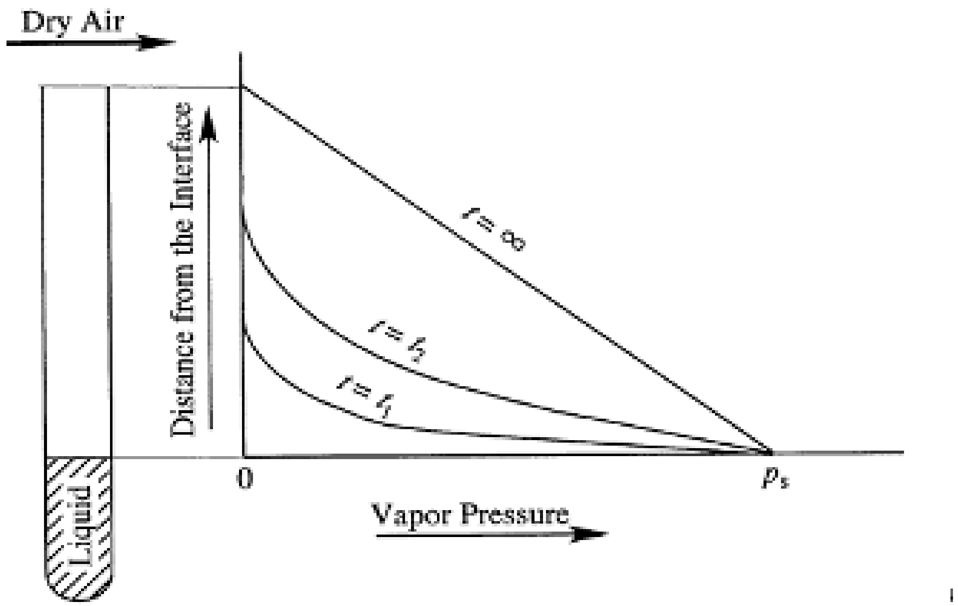
- $D=1/3*(9.5*10^{-8}\ m)*475\ m\ s^{-1}=1.5*10^{-5}\ m^2\ s^{-1}$.

Physical interpretation of diffusion coefficient

- λ↓ when p↑ ($\lambda = kT/\sigma p$) → D↓ w p↑, *i.e.* gas MQs diffuse slowly.
- v_{mean}↑ with T↑ ($v_{\text{mean}} = (8kT/\pi m)^{1/2}$), *i.e.* MQs in a hot sample diffuse faster than in a cool sample.
- As λ↑ when the collision cross-section of the MQs↓ ($\lambda = kT/\sigma p$) → D is greater for smaller MQs.

Summary: Fick’s law of diffusion

- Transfer of material is caused by a non-uniform distribution of concentration
- $J_A = -cD\frac{dx_A}{dy}$
- c[kmol m^{-3}]: molar density



Thermal conductivity (reminder)

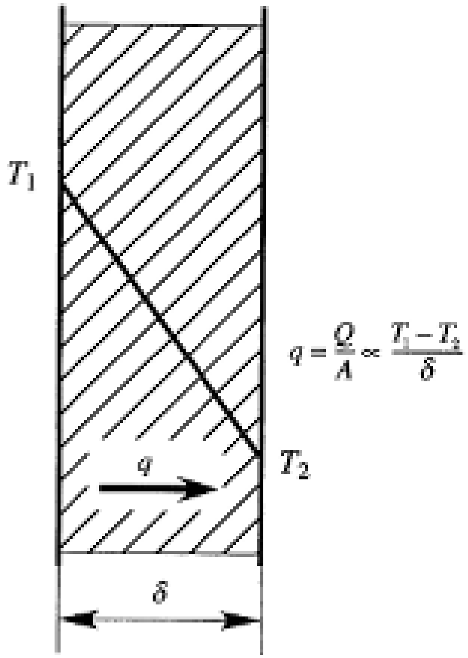
- According to equipartition theorem, each MQ carried an average energy $\varepsilon = vkT$, where v is a number of the order of 1. For atoms, $v = 3/2$.
- When a MQ passes through the imaginary window, it transports that average energy. We assume uniform $\mathcal{N}$ and a T gradient.
- MQs arriving from the left travel a λ from their last collision in a hotter region, and so with higher energy. MQs also arrive from the right after travelling a λ from a cooler region.
- The 2 opposing energy fluxes are: $J(L \rightarrow R) = \frac{1}{4}\mathcal{N}v_{mean}\varepsilon(-\lambda)$ and $J(L \leftarrow R) = \frac{1}{4}\mathcal{N}v_{mean}\varepsilon(\lambda)$, with Z_W.
- The net flux is : $J_z = J(L \rightarrow R) - J(L \leftarrow R) = \frac{1}{4}v_{mean}\mathcal{N}\{\varepsilon(-\lambda) - \varepsilon(\lambda)\} = \frac{1}{4}v_{mean}\mathcal{N}\left\{\left[\varepsilon(0) - \lambda\left(\frac{d\mathcal{E}}{dz}\right)_0\right] - \right.$

Thermal conductivity (reminder)

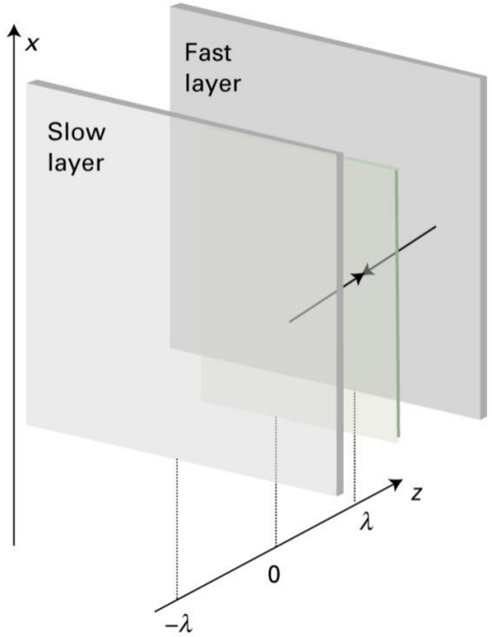
- $\kappa = \frac{1}{3} v v_{mean} \lambda \mathcal{N} k$, thermal conductivity.
- Identifying that $\mathcal{N} = \frac{nN_A}{V} = [J]N_A$, where [J] – molar concentration of J, and noting that vkN_A – molar constant-volume heat capacity of a perfect gas ($C_{V,m} = N_A(\delta\varepsilon/\delta T)_V$), we get $\kappa = \frac{1}{3} v_{mean} \lambda [J] C_{V,m}$.
- Recognising that $\mathcal{N} = p/kT$ and using $D = \frac{1}{3} \lambda\, v_{mean}$: $\kappa = \frac{vpD}{T}$.
- As $\lambda \alpha 1/p$ ($\lambda = kT/\sigma p$) and $\mathcal{N} \alpha p$ ($\mathcal{N} = p/kT$) → $\kappa \alpha (\lambda * p)$ is independent on p.
- κ greater for gases with high heat capacity.

Summary: Fourier’s law of heat conduction

- Heat will be transferred from the hot to the cold surface and this phenomenon is known as the conduction of heat .
- $Q\alpha A\frac{(T_1T_2)}{\delta}$, where δ – thickness of plate
- If δ – infinitesimally small: $q = \frac{Q}{A} = -\kappa\frac{dT}{dy}$
- Q[W]: rate of heat transfer, q[Wm^{-2}]: heat flux



Laminar flow



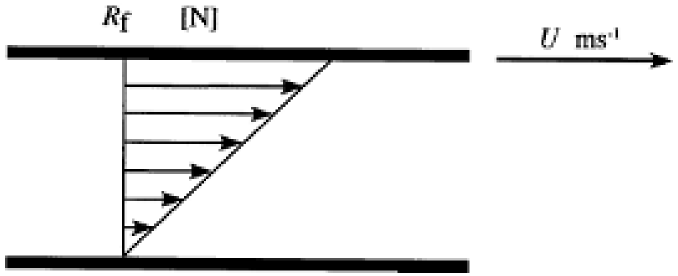
- MQs travelling from a fast layer to a slow layer transport a momentum of $mv_x(\lambda)$ to their new layer at z=0; those travelling the other way transport $mv_x(-\lambda)$.
- Assuming a uniform density, $Z_W = \frac{1}{4}\mathcal{N}v_{mean}$.
- Momentum of MQs arriving from the right: $mv_x(\lambda) = mv_x(0) + m\lambda\left(\frac{dv_x}{dz}\right)_0$, and from the left: $mv_x(-\lambda) = mv_x(0) - m\lambda\left(\frac{dv_x}{dz}\right)_0$.
- The net flux of x-momentum is $J_z = \frac{1}{4}v_{mean}\mathcal{N}\left\{\left[mv_x(0) - \lambda\left(\frac{dv_x}{dz}\right)_0\right] -\right.$

Viscosity

- Similar considerations to diffusion can be made to obtain: $\eta = \frac{1}{3} v_{mean} \lambda m \mathcal{N}$, viscosity.
- Using $mN_A = M$ and $D = \frac{1}{3} \lambda\, v_{mean}$, we get $\eta = MD$[J] or $\eta = pMD/RT$.
- As λ α $1/p$ ($\lambda = kT/\sigma p$) and [J] α p, it follows that η α $\lambda \mathcal{N}$ is independent of p.
- Because v_{mean} α $T^{1/2}$ ($v_{mean} = (8kT/\pi m)^{1/2}$), η α $T^{1/2}$, *i.e.* η of a gas ↑ with T↑.
  - At high T MQs travel quicker so the flux is greater.
  - By contrast, the η of liquids ↓ when T↑ because of intermolecular interactions, which we neglect in a perfect gas.

Summary: Newton’s law of viscosity

- $\tau = \tau_w = R_f/A$, where τ_w – shear stress at the wall, R_f – drag force or frictional drag
- $\tau = -\eta \frac{dv}{dy}$; τ – shear stress; y –distance from wall; A – surface of plate
  - Fluids are classified into 2 groups: Newtonian fluids , which obey Newton’s law of viscosity, and non-Newtonian fluids, which do not obey Newton’s law.
  - Common fluids such as air, water, and oils generally behave as Newtonian fluids, whereas polymer solutions usually behave as non-Newtonian fluids.



Viscosity

- D=1.5*10^{-5} m^2s^{-1} for N_2 at 25 °C.
- Calculate the viscosity of N_2 at 1.0 bar taking into account that M=28.02 g mol^{-1}.

- $\eta = \frac{1}{3} v_{mean} \lambda m \mathcal{N}$

Answer

- $$\eta = \frac{\left(1.0\times10^{5}\,\overset{J\ m^{-3}}{Pa}\right)\times\left(28.02\times10^{-3}\ kg\ mol^{-1}\right)\times\left(1.5\times10^{-5}\ m^{2}s^{-1}\right)}{(8.314\ JK^{-1}mol^{-1})\times(298\ K)} = 1.7\times10^{-5}\ kg\ m^{-1}s^{-1}$$

Motion in liquids

- Liquids are central to industrial chemical reactions and it is crucial to know how the mobility of MQs and solutes in them carries with the conditions.
- Ionic motion is a way of exploring this motion as forces to move them can be applied electrically. From electrical measurements the properties of diffusing neutral MQs may also be inferred.
- Ions reach a terminal velocity when electrical force on them is balanced by the drag due to the viscosity of the solvent (↑ with T↑).
- 2 aspects of motion in liquids will be considered, pure liquids and solutes.

Pure liquids

- Relaxation time measurements in NMR and EPR – mobilities of MQs, *cf.* rotation of large vs small MQs (5° steps vs jumps between different states, respectively);
- Inelastic neutron scattering – motion of particles, internal dynamics of macromolecules;
- Viscosity - $J_z(x - component\ of\ momentum) = -\eta \frac{dv_x}{dz}$
- Unlike in a gas, for MQs to move in a liquid they must acquire a minimum energy (activation energy) to escape from its neighbours
- $\eta = \eta_0 e^{E_a/RT}$, temperature dependence of η.
  - Note +ve sign in exponent as $\eta\ \alpha$ (mobility)$^{-1}$
  - $\eta\downarrow$ with $T\uparrow$!

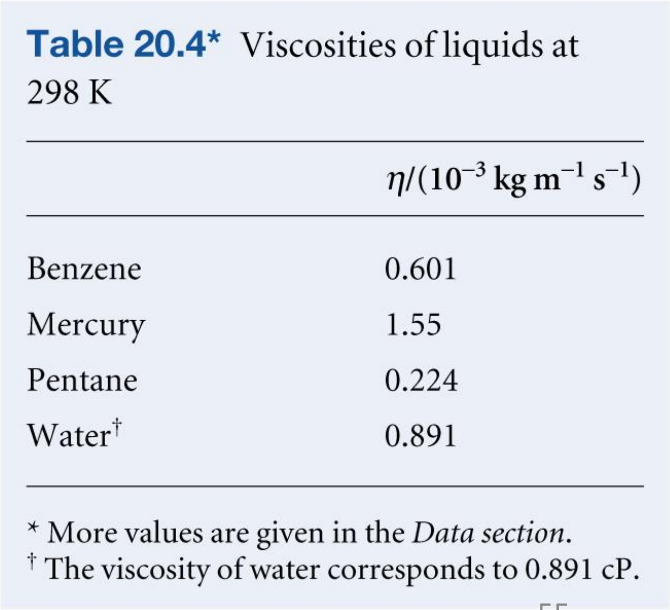


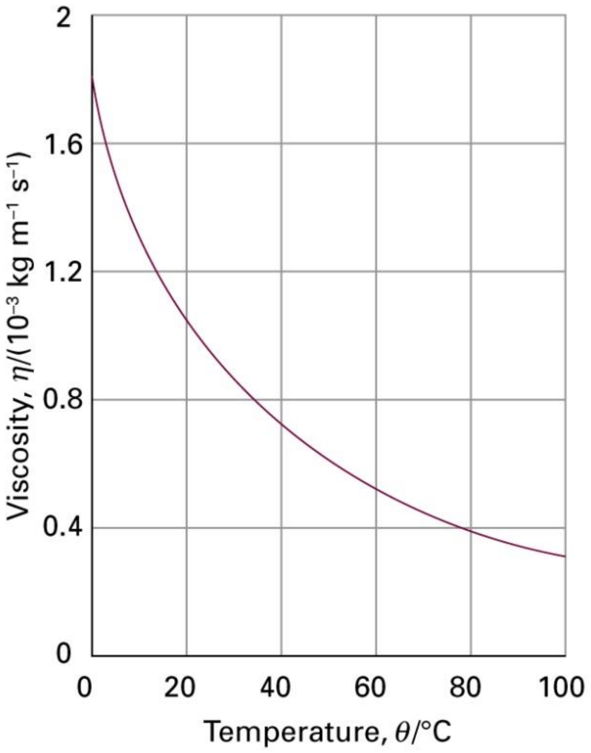
Table 20.4* Viscosities of liquids at 298 K

	$\eta/(10^{-3}\ \mathrm{kg\ m^{-1}\ s^{-1}})$
Benzene	0.601
Mercury	1.55
Pentane	0.224
Water†	0.891

* More values are given in the *Data section*.
† The viscosity of water corresponds to 0.891 cP.

Pure liquids

- One issue is related to the change of density on temperature change.
- Temperature dependence of a liquid when the density is constant (*i.e.* dV=0) is much less than at constant pressure.
- Intermolecular interactions govern the magnitude of E_a.
- Calculating E_a is very complex problem and still unsolved.
- For example, at low T, $\eta(H_2O)\downarrow$ with $p\uparrow$ - this is in line with the rupture of H-bonds.



Liquid viscosity

- $\eta(H_2O)$ at 25 °C and 50 °C is 0.890 mPa s and 0.547 mPa s, respectively.
- Calculate the activation energy for molecular migration.

- $\eta = \eta_0 e^{E_a/RT}$

Answer

- $\frac{\eta(T_2)}{\eta(T_1)} = e^{E_a/R(\frac{1}{T_2} - \frac{1}{T_1})} = \frac{R\ \ln\{\eta(T_2)/\eta(T_1)\}}{\frac{1}{T_2} - \frac{1}{T_1}} = \frac{(8.314\ JK^{-1}mol^{-1})\ \ln\left(\frac{0.547}{0.890}\right)}{\frac{1}{323\ K} - \frac{1}{298\ K}} =$ $1.56 \times 10^4\ Jmol^{-1}$

Electrolyte solutions

- By studying the net transport of charged species through solution – ions may be dragged through the solvent by the application of a potential difference between two electrodes immersed in the sample.
- Through understanding the series of events occurring for charged species it is possible to extrapolate some conclusions for species that are neutral.

Conductivity

- Fundamental measurement to study the motion of ions is the electrical resistance, R, of the solution $[R]=\Omega$.
- The conductance, G, the inverse of resistance; $[G]=\Omega^{-1}$ or S (Siemens).
- The conductance of a sample ↓ w its length (l) and ↑ w its cross-sectional area (A).
- Electrical conductance, the constant κ in $G = \kappa A/l$; $[\kappa]=\mathrm{Sm}^{-1}$.
- Conductivity depends on the # of ions present;
- Molar conductivity, $\Lambda_m = \kappa/c$, c – molar concentration of the electrolyte. $[\Lambda_m] = \mathrm{S\ m^2\ mol^{-1}}$
  - *strong electrolyte*, an electrolyte with a molar conductivity that varies only slightly with concentration.
  - *weak electrolyte*, an electrolyte with a molar conductivity that is normal at concentrations close to zero, but falls sharply to low values as the concentration increases.

Conductivity

- Kohlrausch's law, for the concentration dependence of the molar conductivity of a strong electrolyte at low concentration, $\Lambda_m = \Lambda_m{}^\circ - \mathcal{K}c^{1/2}$.
- $\mathcal{K}$, the Kohlrausch constant depends on the identity of the solute.
- limiting molar conductivity, $\Lambda_m{}^\circ$, the molar conductivity at zero concentration, is the sum of contributions from its individual ions.
- law of the independent migration of ions, $\Lambda_m{}^\circ = v_+\lambda_+ + v_-\lambda_-$
- where λ_+ & λ_-: limiting molar conductivity of cations and anions, respectively, v_+ & v_-: # of cations and anions per formula unit of electrolyte ($v_+ = v_- = 1$ for HCl, $CuSO_4$, $v_+ = 1$ and $v_- = 2$ for $MgCl_2$).

Mobility of ions

- To interpret conductivity measurements we need to know
  - why ions move at different rates,
  - why they have different molar conductivities, and
  - why the molar conductivities of strong electrolytes decrease with the sqrt of the molar concentration.
- Though the motion of an ion remains largely random, the presence of an electric field biases its motion, and the ion undergoes net migration through the solution.
- When the potential difference between the two planar electrodes a distance l apart is $\Delta\varphi$, the ions in the solution between them experience a uniform electric field of $E = \frac{\Delta\varphi}{l}$.
- In such a field an ion of charge *ze* experiences a force of $F = zeE = \frac{ze\Delta\varphi}{l}$.

Stokes’ law

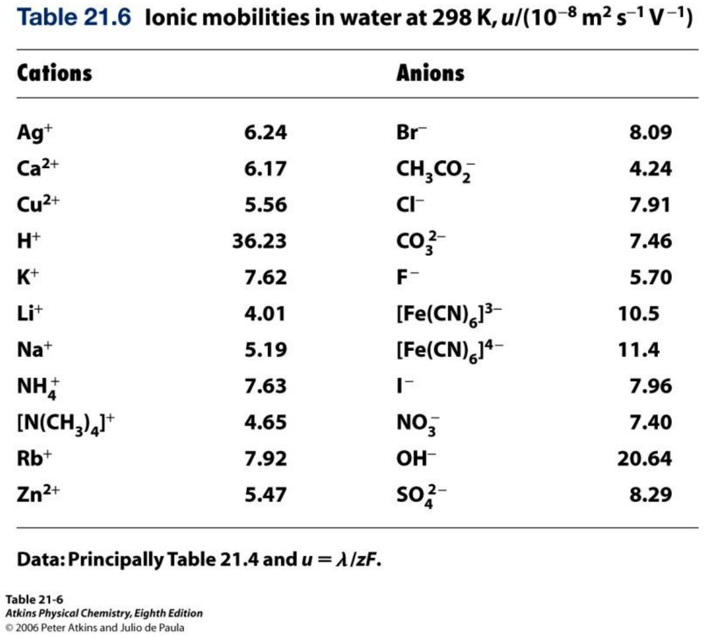


Table 21.6 Ionic mobilities in water at 298 K, $u/(10^{-8}\ m^2\ s^{-1}\ V^{-1})$

Cations		Anions	
Ag^+	6.24	Br^-	8.09
Ca^{2+}	6.17	$CH_3CO_2^-$	4.24
Cu^{2+}	5.56	Cl^-	7.91
H^+	36.23	CO_3^{2-}	7.46
K^+	7.62	F^-	5.70
Li^+	4.01	$[Fe(CN)_6]^{3-}$	10.5
Na^+	5.19	$[Fe(CN)_6]^{4-}$	11.4
NH_4^+	7.63	I^-	7.96
$[N(CH_3)_4]^+$	4.65	NO_3^-	7.40
Rb^+	7.92	OH^-	20.64
Zn^{2+}	5.47	SO_4^{2-}	8.29

Data: Principally Table 21.4 and $u = \lambda/zF$.

Table 21-6
Atkins Physical Chemistry, Eighth Edition

- A cation responds to the application of the field by acceleration to the –ve, an anion by an acceleration to the +ve electrode.
- As the spherical ion of *a* radius moves through the solvent it experiences a frictional retarding force, F_{fric}, α *s*, speed.
- F_{fric} is given by Stokes’ law: $F_{\text{fric}}=fs$, where $f=6\pi\eta a$.
- The 2 forces act in opposite directions and the ions reach a terminal speed, the drift speed: $s = \frac{zeE}{f}$.
- *s* α strength of applied field; $s=uE$, where $u = \frac{ze}{f} = \frac{ze}{6\pi\eta a}$: mobility of ion.

Ion mobility

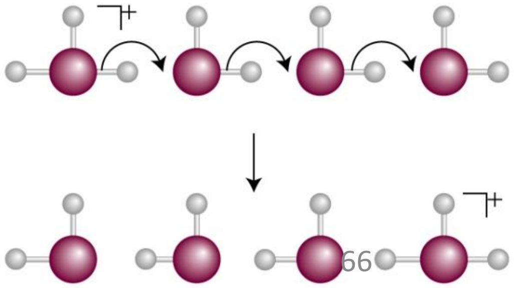
- For an order of magnitude estimate we can take z=1 and a as the radius of an ion such as Cs^+, which is 170 pm.
- Calculate the mobility of Cs^+ if the viscosity of its solution is η=1.0 cP (1.0 mPa)
- $u = \frac{ze}{f} = \frac{ze}{6\pi\eta a}$

Answer

- $$u = \frac{ze}{6\pi\eta a} = \frac{1.6\times10^{19}\ \overset{\text{J V}^{-1}}{C}}{6\pi\times(1.0\times10^{3}\ \underset{\text{J m}^{-3}}{Pa}\ s)\times(170\times10^{-12} m)} = 5.0\times10^{-8}\ m^2V^{-1}s^{-1}$$
- This value means that when there is a potential difference of 1 V across a solution of length 1 cm (so *E*=100 V m^{-1}), the drift speed is typically about 5 µm s^{-1}. That speeds seems slow but not on the MQlar scale where it corresponds to an ion passing about 10^4 solvent MQs per second.

Hydrodynamic radius

- As the drift speed governs the rate at which charged species are transported, conductivity should decrease with viscosity and ion size.
- This is true for bulky ions but not for small ones, where u↑ from Li^+ to Cs^+ even though ionic radius ↑.
- This contradiction may be resolved by understanding a in Stokes' law as the hydrodynamic radius, which takes into account all the H_2O MQs it carries in its hydration shell.
    - Small ions give rise to stronger electric fields than large ones so small ions are more extensively solvated.
- H^+ though small has a very high mobility. According to the Grotthuss mechanism. there is an effective motion of a proton that involves the rearrangement of the protons in a group of water MQs.

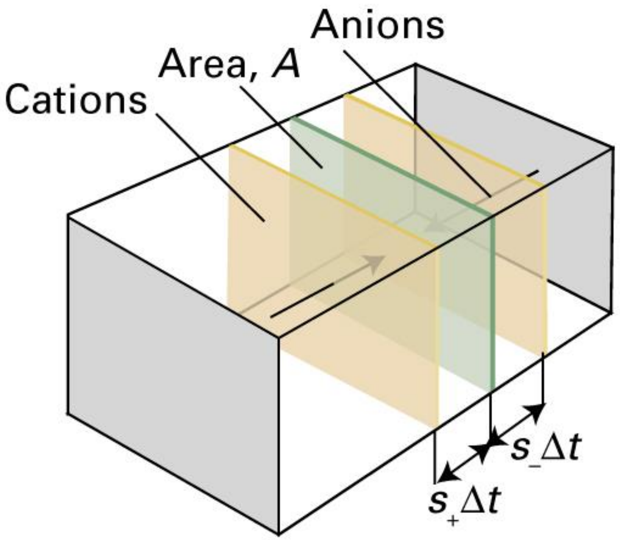


Mobility and conductivity

- **ionic conductivity,** the contribution of ions of one type to the molar conductivity: $\lambda = zuF$,

where F=9.648*10^4 Cmol^{-1},

the Faraday constant.



molar conc. of each type of ion $= vc$

$\#$ density $= vcN_A$

$\#$ of ions in $s\Delta tA = vcN_A s\Delta tA$

$$J(ions) = \frac{vcN_A s\Delta tA}{\Delta tA} = vcN_A s$$

$$J(\text{charge}) = J(ions) \times ze = ze \times vcN_A s = zvcsF \xrightarrow{s=u\mathcal{E}} zvcu\mathcal{E}F$$

$$I = JA = zvcu\mathcal{E}FA \xrightarrow{\mathcal{E}=\Delta\phi/l} \frac{zvcuFA\Delta\phi}{l}$$

$$I = \frac{\Delta\phi}{R} = G\Delta\phi = \frac{\kappa A\Delta\phi}{l}$$

Potential difference by Ohm's law

$G = \kappa A/l$

$$\therefore \kappa = zvcuF \xrightarrow{\Lambda_m=\kappa/c} \kappa/vc = \lambda = zuF$$

$$\Lambda_m^0 = v_+\lambda_+ + v_-\lambda_- = (v_+z_+u_+ + v_-z_-u_-)F$$

Applies for cations & anions so solution is in the limit at 0 concentration

- **Kohlrausch's law,** $\Lambda_m = \Lambda_m{}^\circ - \mathcal{K}c^{1/2}$ **ion–ion interactions**

Ionic conductivity

- The typical ionic mobility may be estimated as $5.0*10^{-8}$ $m^2V^{-1}s^{-1}$.
- If z=1 for both the cation and the anion, what would the typical limiting molar conductivity be?

- $\lambda = zuF$
- $F=9.648*10^4$ $Cmol^{-1}$

Answer

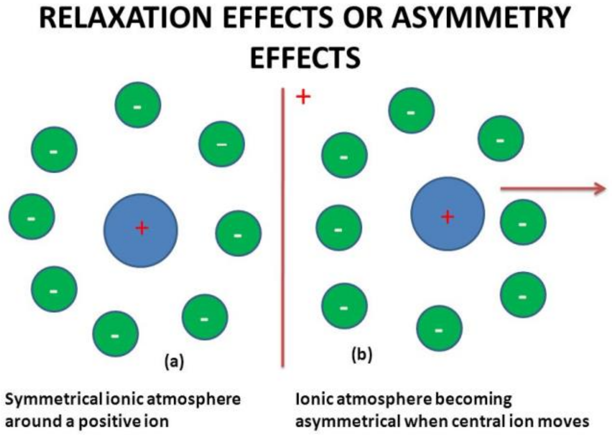
- λ = zuF=$(5.0*10^{-8}\ \text{m}^2\text{V}^{-1}\text{s}^{-1})*(9.648*10^{4}\ \overset{\text{J V}^{-1}}{\text{C}}\text{mol}^{-1})=$

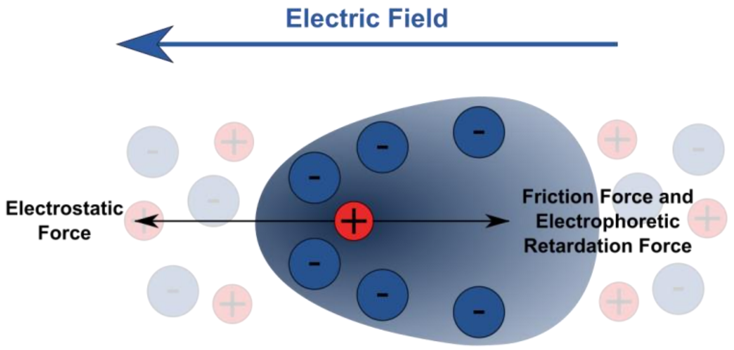
  $4.8*10^{-3}\ \text{m}^2\text{V}^{-1}\text{s}^{-1}\text{Cmol}^{-1}$

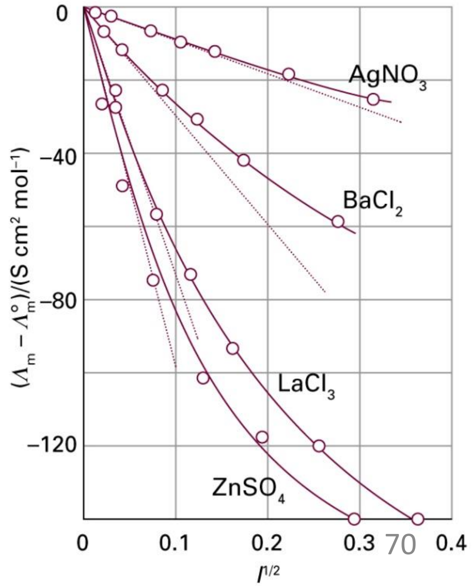
Ion-ion interactions

- relaxation effect: the reduction of an ion’s mobility due to distortion of the ionic atmosphere.
- electrophoretic effect: the enhanced viscous drag due to the counter current of oppositely charged ions.
- Debye–Hückel–Onsager theory: a theory of the concentration dependence of the molar conductivity of a strong electrolyte, $K = A + B\Lambda_m^\circ$.

$$\Lambda_m = \Lambda_m^\circ - \mathcal{K}c^{1/2}$$

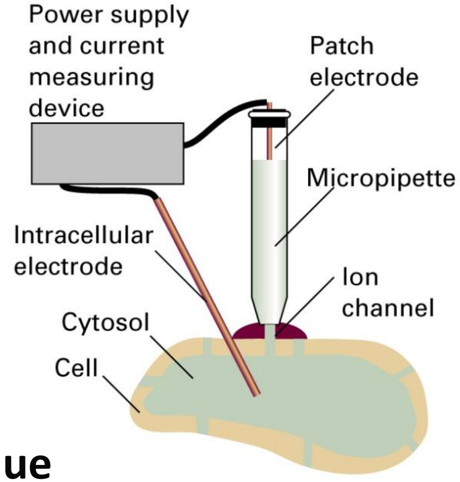






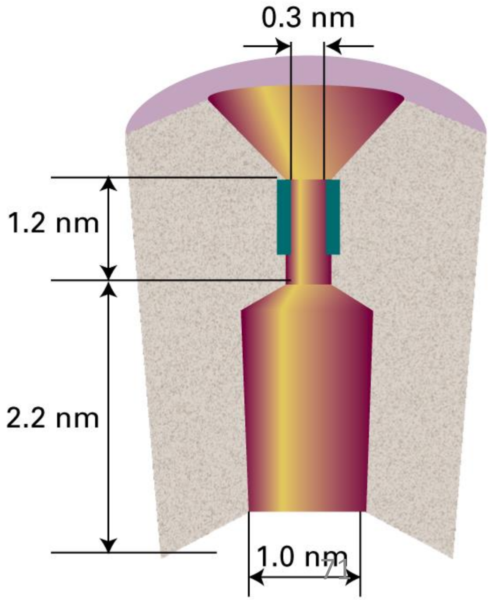
Ion channel

- passive transport: the tendency for a species to move spontaneously down a concentration or potential gradient.
- active transport: transport that must be driven by an exergonic process.
- channel former: a protein that creates a hydrophilic pore in a membrane.
- ion channel: a protein that effects the movement of a specific ion down a potential gradient.
- ion pump: proteins that effect the active transport of ions.
- patch clamp technique: for studying ion transport across biological membranes.



patch clamp technique

K$^+$ channel



Einstein relations

- An important relation between *s* and the thermodynamic force, *F*, acting on any kind of particle is $s = \frac{DF}{RT}$.
- An ion in solution has $s=uE$, in the presence of an electric field of strength E, and experiences a $F=N_A zeE$.
- Using $N_A e=F$ we get $uE=DFzE/RT$, so $u = \frac{zDF}{RT}$, Einstein relation.
- $\lambda = zuF = \frac{z^2DF^2}{RT}$, for each type of ion.
- From $\Lambda_m^0 = v_+\lambda_+ + v_-\lambda_-$ $\quad \Lambda_m^0 = (v_+z_+^2D_+ + v_-z_-^2D_-)\frac{F^2}{RT}$, Nernst-Einstein equation.

Einstein relations

- $u = ez/f$ and $u = zDe/kT$ relate the mobility in a frictional force and to the diffusion coefficient, respectively.
- Combined: $D = \frac{kT}{f}$, Stokes-Einstein equation
- Using Stokes' law: $D = \frac{kT}{6\pi\eta a}$.

Mobility and diffusion

- $u(SO_4^{2-})=8.29*10^{-8}\ m^2V^{-1}s^{-1}$.
- Determine the diffusion coefficient at 25 °C.

- $u=zDe/kT$

Answer

- $\mathrm{D}=uRT/zF=(8.29*10^{-8}\ \mathrm{m^2V^{-1}s^{-1}})*(8.3145\ \mathrm{JK^{-1}mol^{-1}})*(298\ \mathrm{K})/\{2*(9.649*10^{4}\ \mathrm{C\ mol^{-1}})\}$

$\mathrm{J\ V^{-1}}$

Any questions?