The criterion kT for gauging the IA strength

- IA energy > kT wins out over disorganizing thermal motion

How strong is the intermolecular attraction to condense molecules to a liquid at a specific T and p?

— T = 273 K, p = 1 atm

$V_{gas} = 22{,}4\ l\ mol^{-1}$ $\quad V_{liquid\ typical} \sim 20\ cm^3$

Gas and liquid in equilibrium: equal chemical potentials!

$$\mu^i_{gas} + kT \log X_{gas} = \mu^i_{liquid} + kT \log X_{liq}$$

with $\mu^i_{liq} \gg \mu^i_{gas} \Leftrightarrow \mu^i_{gas} - \mu^i_{liq} \approx \mu^i_{liq}$

$$= kT \log \frac{X_{liq}}{X_{gas}}$$

$$\approx kT \log \frac{22400}{20} \approx 7\,kT$$

if gas obeys the ideal gas law:

between 100 – 500 K, the log term changes only ~13%.

$\Rightarrow \mu^i_{liq} \sim 7\,kT_B$ → boiling temperature or $-N_0\,\mu^i_{liq}/T_B \approx 7 N_0 k \approx 7 R$

– Boiling point is simply proportional to the energy needed to take a molecule from liquid to vapor

U_{vap} = ~~[scribbled]~~ $- N_0 \mu^i_{liq}$, the enthalpy of vaporization $H_{vap} = H_{vap}$
energy of vaporization

(latent heat of vap) $= U_{vap} + PV$

$\approx U_{vap} + RT_B$

$$\Rightarrow L_{vap}/T_B \approx (U_{vap}/T_B) + R \approx 7R + R = 8R \approx 70\,J\,K^{-1}\,mol^{-1}$$

⇒ empirical ~~[scribbled]~~ Trouton's rule

$$L_{vap}/T_B \approx 80\ J\,K^{-1}\,mol^{-1}$$

⇒ If cohesive energy $\mu^i > 9kT$ ⇒ condensation of molecules will take place

From above: $\mu^i \approx 6w(\sigma)$

pair interaction energy $> \frac{3}{2}kT$ ⇒ condensation liquid→solid

$\frac{3}{2}kT$ can be used as standard reference for cohesive energy (but is dependent on pressure!)

Boltzmann was so far used as means to find a spatial density distribution of molecules in different regions of a system but it is also possible to determine an orientational distribution.

$W(r) \rightarrow w(\Theta, r)$ Θ = orientation angle

$$X(\Theta_2) = X(\Theta_2) \exp\left(-\frac{w(r,\Theta_2) - w(r,\Theta_1)}{kT}\right)$$

kT: strength of orientation-dependent interactions needed to align molecules mutually

Problems / Discussions?

Strong intermolecular forces covalent and Coulomb interactions

- covalent bonds: tightly bind atoms together to molecules

  (electrons are shared)

  * valency, directionality
  * short of range: 0,1 – 0,2 nm, 100 – 300 kT per bond (200 – 800 kJ mol^{-1})

    decrease with bond length

    $C \equiv N$ 800 kJ mol^{-1}

Coulomb Force:

$$F = -\frac{dw(r)}{dr} = \frac{Q_1 Q_2}{4\pi \varepsilon_0 \varepsilon r^2} = \frac{z_1 z_2 e^2}{4\pi \varepsilon \varepsilon_0 r^2}$$

like charges: F positive ⇝ repulsive
unlike " : F negative, attractive

electric field at a distance r from a charge Q_1

$$E_1 = \frac{Q_1}{4\pi \varepsilon_0 \varepsilon r^2} \quad [V m^{-1}]$$

this field, acting on a second charge, gives rise to a force $F = E_1 Q_2 = \dfrac{Q_1 Q_2}{4\pi \varepsilon \varepsilon_0 r^2}$

Strength for two isolated ions in contact, Na^+, Cl^-:

$$w(r) = \frac{-(1{,}602 \cdot 10^{-19})^2}{4\pi\,(8.854 \cdot 10^{-12})(0{,}276 \cdot 10^{-9})} = 8.4 \cdot 10^{-19}\ J$$

kT @ 300 K: $4.1 \cdot 10^{-21}$ J : ~ 200 kT per ion pair in vacuum

similar to covalent bond!!

$w(r > 56\ nm) < kT$, long range!
Coulomb
very strong!

| Worked example -- kind of it!! |

Ionic crystals

- Coulomb forces: hold Na^+, Cl^- ions together: 'ionic bond'
- isolated pair energy of Na^+Cl^-: too simplistic due to long-range interactions: not only nearest-neighbor interactions! Coulomb energy of one ion with all other ions in the lattice has to be summed

NaCl: Na^+ has six nearest Cl^- neighbors, $r = 0{,}276$ nm

12 next-nearest " Na^+, at $\sqrt{2}\,r$

8 more Cl^- at $\sqrt{3}\,r$ etc.

Total interaction energy for a pair $Na^+ - Cl^-$

$$\mu^i = -\frac{e^2}{4\pi\varepsilon_0 r}\left[6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{2} + \dots\right]$$

$$= \frac{-e^2}{4\pi\varepsilon_0 r}\left[6 - 8.485 + 4{,}619 - 3 + \dots\right]$$

$$= \underline{1{,}748}\;\frac{e^2}{4\pi\varepsilon_0 r} = -1{,}46 \cdot 10^{-18}\,J$$

Madelung constant; depends on the nature of the ions

Molar lattice energy: $\times N_0$

$\updownarrow$ $U = -N_0\mu^i = 6.02 \cdot 10^{23} \cdot 1{,}46 \cdot 10^{-18} = 880$ kJ mol^{-1}

15% higher than measured value: contains no repulsive term (very short range) from RbI to LiF ; 600 - 1000 kJ mol^{-1}

Reference States

- ions form a condensed phase : reference $r = \infty$
  vacuum $\varepsilon = 1$

  ↳ energy of ionic crystals does not contain ε of the medium (NaCl : $\varepsilon \approx 6$)

- Ions interact in a condensed liquid medium.

  $r = \infty$ as reference,
  ε (solvent) has to be considered (interaction occurs entirely in the solvent medium!!

Range of Coulomb force

- $\sim \frac{1}{r^2}$ dependence : very long ranged
  (same as gravitational)
  force

- contradiction to the earlier statement that intermolecular force laws must fall faster than $\frac{1}{r^4}$ ($\frac{1}{r^3}$ for energy)

- Counterions (electroneutrality) screen electric field of ions ↳ decay more rapidly

Born energy of an ion

- Single ion in vacuum or a medium:
  has an electrostatic free energy: work done in forming the ion

- vacuum: self energy
- medium: Born or solvation energy

} of an ion

→ determines solubility, partitioning between solvents!

Charging an ion or sphere to the full charge Q

- from zero, increment dq, at any stage charge = q
- work done in putting this charge from infinity to r = a

Coulomb: $dw = \frac{q \, dq}{4\pi\varepsilon\varepsilon_0 a}$ (q → Q_1, dq → Q_2, a → r)

↳ total free energy to charge the ion (Born energy)

$$\mu^i = \int dw = \int_0^Q \frac{q\,dq}{4\pi\varepsilon\varepsilon_0 a} = \frac{Q^2}{8\pi\varepsilon\varepsilon_0 a} = \frac{(z \cdot e)^2}{8\pi\varepsilon\varepsilon_0 a}$$

→ related to ε of the medium

→ positive: unfavorable, since it keeps the charge on the sphere against repulsion