Systematic error
in the Langevin reduction
of ion mobilities

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THE PERSONAL MOTIVATION OF THE RESEARCH

We are measuring the natural air ion mobilities and studying the correlation between air pollution and ion mobility spectra. The composition of cluster ions in atmospheric air depends on the trace admixtures in the air and on temperature. The mobility variation has two factors:

1) temperature variation of the air ion composition,
2) temperature variation of the mobility at given composition.

The first factor is a subject of our research. Unfortunately, only the composite effect is available in measurements. Thus the knowledge about the second factor is required.

THE LANGEVIN RULE

Traditionally, the measurements of mobility are numerically reduced to the standard conditions according to the Langevin rule

$$K_{\text{reduced}} = K_{\text{measured}} \frac{273.15\,\text{K}}{T} \frac{p}{101325\,\text{Pa}}$$

and presented in publications without any notice about the method of reduction. It is well known that the Langevin rule is correct only in the limit of zero-size ions and considerable errors are possible when applying the rule to the cluster ions. However, the Langevin rule is still used in practice and often considered as an conventional operation without claiming the results as real mobilities at standard conditions. This approach seems to be problematic and even misleading. An example: The variation of the published experimental data about mobilities of some simple molecular ions (e.g. O_2^- in nitrogen) essentially exceeds the estimated measuring errors. The measurements have been made at different temperatures and results are published as reduced according to the Langevin rule.

We will characterize the error of the Langevin rule using an approximation

$$K = \text{const}\,\frac{T^\tau}{p^\psi}$$

in a narrow range of temperature and pressure, and considering parameters τ and ψ as functions of temperature and pressure:

$$\tau = \frac{\text{d}K}{\text{d}T} \frac{T}{K}, \qquad \psi = -\frac{\text{d}K}{\text{d}p} \frac{p}{K}$$

According to the Langevin rule, $\boxed{\tau = \psi = 1}$

FREE   **MOLECULE**   **REGIME** (Chapman, Enskog)

elementary charge   mass of gas molecule   mass of ion

$$K_{\text{free molecule}} = \frac{3e}{8n_{\text{g}}\Omega^{(1,1)}} \sqrt{\frac{\pi(1 + m_{\text{g}}/m_{\text{i}})}{2m_{\text{g}}kT}}$$

number concentration of molecules   first collision integral   Boltzmann constant   absolute temperature

The polarization limit

$$K_{\text{Langevin}} = 0.5105 \frac{e}{n_{\text{g}}} \sqrt{\frac{\varepsilon_{\text{o}}(1 + m_{\text{g}}/m_{\text{p}})}{\alpha m_{\text{g}}}}$$

follows the mobility is inversely proportional to the gas density and the values of the variation parameters are $\tau = \psi = 1$ (the Langevin rule).

LARGE IONS (Stokes, Cunningham, Knudsen, Weber, Millikan)

mean free path of gas molecules   the slip factor coefficients ($a = 1.2$, $b = 0.5$, $c = 1$)

$$K_{\text{Millikan}} = e \frac{1 + \frac{l}{r}\left[a + b\exp\left(-c\frac{r}{l}\right)\right]}{6\pi\eta r}$$

gas viscosity   ion radius

The big particle limit: $\tau = -0.8$, $\psi = 0$.

The fine particle limit:

$$K_{\text{Millikan}\to 0} = \frac{e(a+b)l}{6\pi\eta r^2} \qquad \frac{l}{\eta} = \frac{1.256}{p}\sqrt{\frac{kT}{m}}$$

gives $\tau = 0.5$, $\psi = 1$.

FREE MOLECULE REGIME

elementary charge   mass of gas molecule   mass of ion

$$K_{\text{free molecule}} = \frac{3e}{8n_g \Omega^{(1,1)}} \sqrt{\frac{\pi(1 + m_g / m_i)}{2m_g kT}}$$

number concentration of molecules   first collision integral   Boltzmann constant   absolute temperature

Neutral rigid spheres: $\Omega^{(1,1)} = \pi\delta^2$ (δ = the collision distance).

Charged rigid spheres and (∞–4) potential:

$$\Omega^{(1,1)} = \Omega^{(1,1)*}\pi\delta^2, \quad \Omega^{(1,1)*} = f(T^*), \quad T^* = \frac{kT}{U(\delta)}, \quad U(\delta) = \begin{cases} \text{if } r < \delta \text{ then } \infty \\ \text{if } r > \delta \text{ then } \dfrac{-\alpha e^2}{8\pi\varepsilon_\circ r^4} \end{cases}$$

Approximation:

$$f(T^*) = \begin{cases} \text{if } T^* \leq 1 \text{ then } 1.4691 \times T^{*-1/2} - 0.341 \times T^{*-1/4} + 0.185 \times T^{*5/4} + 0.059 \\ \text{if } T^* \geq 1 \text{ then } 1 + 0.106 \times T^{*-1} + 0.263 \times T^{*-4/3} \end{cases}$$

IMPROVEMENTS (Tammet, H., *J. Aerosol Sci., 26*, 459–475, 1995)

1) $\delta = \delta(T)$ (Chapman, Hainsworth, 1924)

2) Electrical compression $T_\delta = \dfrac{E_{def}}{k} = T + \dfrac{|U_{pol}(\delta)|}{k}$

3) Inelastic collisions $\Omega^{(1,1)} = s(r_i, T_\delta)\pi\delta^2$

ion mass radius

$$r_i = \sqrt[3]{\frac{3m_i}{4\pi\rho}}, \quad \rho - \text{density of ionic matter (the first ill-determined parameter)}$$

$$s = \begin{cases} 1.00 & \text{for } r \to 0 \\ 1.32 & \text{for } r \to \infty \text{ (empirical value, Millikan, 1923)} \\ 1.393 & \text{for full temperature accommodation (Epstein, 1924)} \end{cases}$$

SYNTHETIC SEMIEMPIRICAL MODEL (modified Millikan equation)

mean free path
of gas molecules

the slip factor coefficients
($a = 1.2$, $b = 0.5$, $c = 1$)

$$K = f_1 f_2 e \frac{1 + \dfrac{l}{\delta}\left[a + b\exp\left(-c\dfrac{\delta}{l}\right)\right]}{6\pi\eta\delta}$$

gas viscosity

collision distance

$$\delta = r_i + h_{(T_\delta)} + r_g(T_\delta)$$

h – extra distance (the second ill-determined parameter).

$$f_1 = \sqrt{1 + \frac{m_g}{m_i}}$$

$$f_2 = \frac{2.25}{(a+b)\left(\Omega^{(1,1)*}_{\infty-4}(T^*) + s(r_i, T_\delta) - 1\right)}$$

When $r_m \to 0$ the model approaches the free molecule regime equation with

$$\Omega^{(1,1)} = \left[\Omega^{(1,1)*}_{\infty-4} + s(r_i, T_\delta) - 1\right]\pi\delta^2$$

FACTOR $s(r_i, T_\delta)$

Two assumptions:

1) The melting of internal degrees if freedom of the particle energy is described by the Einstein factor:

$$\frac{x^2 e^x}{(e^x - 1)^2} \quad \text{where} \quad x = \frac{\Delta E}{kT}$$

2) the average separation of internal energy levels is inversely proportional to the number of atoms

$$\Delta E = \frac{\text{const}}{r_i^3}$$

It follows the model $\quad s = 1 + (s_\infty - 1)x^2 \dfrac{e^x}{(e^x - 1)^2} \quad \text{where} \quad x = \dfrac{273\,\text{K}}{T}\left(\dfrac{r_{cr}}{r_i}\right)^3.$

r_{cr} – critical radius (the third ill-determined parameter).

FITTING OF THE MODEL TO THE EMPIRICAL DATA

Kilpatrick, W.D. (1971) An experimental mass-mobility relation for ions in air at atmospheric pressure. *Proc. Annu. Conf. Mass Spectrosc. 19th.* 320-325.

(mass interval of 35–2122 u)

Böhringer, H., Fahey, D.W., Lindinger, W., Howorka, F., Fehsenfeld, F.C., and Albritton, D.L. (1987) Mobilities of several mass-identified positive and negative ions in air. *Int. J. Mass Spectrom. Ion Processes* **81**, 45-65.

$$\sigma_{rel} = \sqrt{\frac{1}{n}\sum_{i=1}^{n}\left(\frac{K_{\text{model}} - K_{\text{emp}}}{K_{\text{emp}}}\right)^2} = f(\rho, h, r_{cr}) \quad \rightarrow \quad \min = 2.59\%$$

$$\boxed{\rho = 2.07\ \text{g cm}^{-3}, \quad h = 0.115\ \text{nm}, \quad r_{cr} = 1.24\ \text{nm}}$$

$$(\rho_{\text{sphere}} = 2.07 \ \Rightarrow \ \rho_{\text{cubic lattice}} = 1.08)$$

EXAMPLE

The air ion mass-mobility correlation has been measured by Kilpatrick at 200ºC, and the mobilities have been published as reduced to standard conditions using the Langevin rule. The fitting of these data yields a regression equation (CRC Handbook, 1993)

$$K \approx \left(\sqrt[3]{\frac{850 \text{ u}}{m}} - 0.3 \right) \text{cm}^2\text{V}^{-1}\text{s}^{-1} \qquad m \approx \frac{850 \text{ u}}{\left(0.3 + K\text{:cm}^2\text{V}^{-1}\text{s}^{-1} \right)^3}$$

When the original 200ºC data were restored and the mobilities at 0ºC were recalculated according to the new model, the best fit is achieved at different coefficients of the equation

$$K \approx \left(\sqrt[3]{\frac{1200 \text{ u}}{m}} - 0.2 \right) \text{cm}^2\text{V}^{-1}\text{s}^{-1} \qquad m \approx \frac{1200 \text{ u}}{\left(0.2 + K\text{:cm}^2\text{V}^{-1}\text{s}^{-1} \right)^3}$$

The ratio of air ion masses estimated according to different approximations is

$$\frac{1200}{850}$$

A REPLACEMENT FOR THE LANGEVIN RULE (???)

ReducedMobility :=

  1.602 * Mobility (28.96, 0.00171, 0.3036, 44, 0.8, 1013.25, 273.15, 2.07, 1,

    MassDiameter (millibar, 273.15 + Celsius, 2.07, 1, MeasuredMobility / 1.602));