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Exponentials - review

Exponentials and logarithms have important properties of value in understanding science, and this is a brief review of some of the rules in handling them.

(1) *Simple rules:*

$y = \log x$, then $x = 10^y$; $y = \ln x$, then $x = e^y$

$e^{\ln x} = x$; $e^{-\ln x} = 1/x$

for example, in "leak" paper, the term $e^{-\ln (C_p/C_1)} = (C_1/C_p)$

Rules of multiplication, etc:

e^x times $e^y = e^{(x+y)}$; $e^x / e^y = e^{(x-y)}$

$\ln (ab) = \ln a + \ln b$; $\ln (a/b) = \ln a - \ln b$

(2) *pH*: pH $\equiv -\log a_{H+}$, where a_{H+} refers to "thermodynamic activity of hydrogen ion", which may equal "molal concentration" to within a few percent. We normally approximate $a_{H+} \sim [H^+]$, and write pH = $-\log [H^+]$. Note from (1) that $[H^+] = 10^{-pH}$.

The "p" in pH stands for the operation "negative logarithm of". Recall that we also have pK_a , where K_a is the acid dissociation constant in the reaction $HA \Leftrightarrow H^+ + A^-$. Thus, $pK_a = -\log K_a$

(3) *Two different logarithms:* Logarithm (base 10, abbreviated log) is convenient in many ways. For example, at pH = 7 , we know that $[H^+] \sim 10^{-7}$ M (0.1 μM). Natural logarithms (base e, abbreviated ln) are "natural" because they fall out of calculus. Let $y = e^{-x}$. The derivative $dy/dx = -e^{-x}$, which is the tangent to the curve at each value of x. The derivative $d(\ln x)/dx = 1/x$.

Log/ln relations can be derived from the rules in (1):

$\ln x = (\ln 10)(\log x) = 2.3026 \log x$; and $10^x = e^{2.3026x}$

(4) *Important approximations:*

e^x may be expressed as a polynomial using the Taylor's expansion :

$e^x = 1 + x + x^2/2 + x^3/3 + ...$ etc.

When x is very small, $x^2/2 << x$, and all higher order terms are even smaller; therefore $e^x \sim 1 + x$ when $x << 1$. (For example, if $x = 0.05$, $e^x = 1.0513$)

Similarly, ln (1 + a) ~ a, if a << 1. Therefore ln (n + Δn) = ln n(1 + Δn/n) ~ ln n + Δn/n, if Δn << n.

(5) *Graphing functions:*

You should be familiar with the way exponential functions *look* when plotted. Calculate and plot these functions:

(a) $J = J_o e^{u/2}$ where J_o is the flux at u = 0 and $u \equiv F\Delta\Psi/RT$. (Note that this equation uses a positive sign for $\Delta\Psi$). Use $J_o = 1$. Calculate values for J at 20 mV intervals from 120 mV to and including 200 mV. Plot the data in the same range. Also plot ln J vs u.

(b) Boltzmann equation: $P(\Delta\mu'')/P(0) = e^{-\Delta\mu''/RT}$

Calculate and plot $P(\Delta\mu'')/P(0)$ versus $\Delta\mu''$, for $\Delta\mu''$ = 0.2, 0.5, 0.8, 1.1, 1.5, 2, 4, 6 kJ/mol.

Boltzmann Distribution

The system: Consider a closed system consisting of a solution containing solutes that include an ion, j. This is a homogeneous solution at equilibrium (with itself). We may write for the chemical potential of ion j:

$$\mu_j = \mu_j^o + RT \ln c_j$$

where c_j is the concentration of ion "j", and μ_j^o is the standard chemical potential of j. Note that the electrical term, $F\Delta\Psi$, does not appear, because we have only a single aqueous phase - an internal electric field cannot exist in a closed salt solution.

Although the system is at equilibrium, we know that individual ions will, from time to time have energies different from μ_j, due to collisions with neighbors, for example. We will consider ions at two different energies :

$$\mu_j' = \mu_j^o + RT \ln c_j'$$

$$\mu_j'' = \mu_j^o + RT \ln c_j''$$

where c_j' and c_j'' are the concentrations of ion j at these two energies. Combining these equations,

$c_j'' / c_j' = e^{-\Delta\mu/RT}$

where $\Delta\mu = \mu_j'' - \mu_j'$

Note the resemblance to a partition coefficient between TWO phases. This is a partition coefficient within ONE phase between two different energies.

Now, we rearrange equation and divide both sides by c_j^o , which is the TOTAL concentration of j in the solution.

$$(c_j'' / c_j^o) = (c_j' / c_j^o) \quad e^{-\Delta\mu/RT}$$

At this point, note that μ_j'' and μ_j' refer to ANY energies that exist within the solution. Therefore, we may let $\mu_j' = \mu_j$, the *equilibrium* energy of the solution. $\Delta\mu = \mu_j'' - \mu_j$ is therefore the extra energy achieved by the ion relative to the overall energy of the solution.

The concentration fractions have the meaning,

$(c_j'' / c_j^o) = P(\Delta\mu'')$, the fraction or probability of finding an ion at energy μ_j'', and
$(c_j' / c_j^o) = P(0)$, the probability of finding an ion at the average energy, μ_j.

Therefore,

$$P(\Delta\mu'') = P(0) \; e^{-\Delta\mu''/RT}$$

This is the Boltzmann equation.