Freezing-Point Depression

A. Simple Picture for Strong Electrolytes

1. *Colligative Property*: depends only on *amount* of solute, not its nature. Does depend on *solvent.*

2. *Equation*: $\Delta T_f = -k_f\, m_B\, \nu$ [m_B is solute molality, $k_f =$ 1.860 K kg/mol for water; $\nu = ?$]

3. *Example*: $CaCl_2(s) \rightarrow Ca^{2+}(aq) + 2\,Cl^-(aq)$ $\nu = 3$

   valid because $CaCl_2$ is strong electrolyte, fully ionized in solution.

B. Exact Treatment

$$\ln a_A = \frac{\Delta H_{m,fus}}{R}\frac{\Delta T_f}{T_f^*\, T_f} \approx \frac{\Delta H_{m,fus}}{R\, T_f^{*2}}\,\Delta T_f$$

$a_A = $ *activity*; **all** quantities refer to solvent properties.

1. $a_A = \gamma_A\, x_A$ (activity coef. × mole fraction)

2. $x_A = n_A/(n_A + \nu\, n_B)$ (defines solvent mole fraction)

3. a_A and γ_A describe deviation of actual system from predictions of simple equation (for which $\gamma_A = 1$). Thus, measurement of ΔT_f permits calculation of γ_A.

C. Alternative (but Equivalent) Approach

$$\phi = \frac{-\ln a_A}{M_A\, \nu\, m_B}$$

defines *practical osmotic coefficient ϕ.* M_A is molar mass of solvent A (kg/mol).

$$\Delta T_f = -k_f\,(\nu\,\phi)\, m_B$$

exact version of 1st equation; ϕ plays role of fudge factor needed to achieve agreement. Product $\nu\phi$ known as *van't Hoff i factor*. Also, have

$$k_f = \frac{R\, T_f^{*2}\, M_A}{\Delta H_{m,fus}}$$

D. Experiment.
For HCl, measure ΔT_f with thermistor, m_B by titration; calculate ϕ, a_A, x_A, and γ_A.

E. Weak Electrolytes

1. *Example*: $HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$ (weak acid)

2. Let m = starting molality of HA and α = fractional ionization. Then at equilibrium $m_{HA} = m\,(1 - \alpha)$, and

$$m\,(1-\alpha) + m\,\alpha + m\,\alpha = m\,(1+\alpha) \equiv m'$$
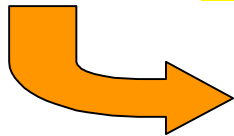
$$K_m = \frac{m\,\alpha^2}{(1-\alpha)} = \frac{(m'-m)^2}{2m - m'}$$

3. *Approach*:   Get m' from ΔT_f using simple eqn., m from titration.   Calculate K_m. Extrapolate to zero ionic strength to get "true" K,

$$\ln K_m = \ln K_a^\circ - 2 \ln \gamma_\pm$$

$$\ln K_m = \ln K_a^\circ + 2.26\,(\alpha\,m)^{1/2}$$

F. Mustering the Data

	3 #	4 T-t'std	5 t-corc	6 m-samp	7 v-tit	8 nB	9 mass-B	10 mass-A
0	1	-0.83500	-0.82813	9.873	28.73	0.0022679	0.082692	0.0097903
1	2	-0.68300	-0.67443	10.010	23.97	0.0018922	0.068991	0.0099410
2	3	-0.51200	-0.50153	9.986	17.92	0.0014146	0.051578	0.0099344
3	4	-0.35000	-0.33772	9.989	12.20	0.00096307	0.035114	0.0099539
4	5	-0.24000	-0.22650	10.010	8.22	0.00064889	0.023659	0.0099863
5	6	-0.16400	-0.14965	10.009	5.57	0.00043970	0.016032	0.0099930
6	7	-0.12400	-0.10920	9.972	4.03	0.00031813	0.011599	0.0099604
7		-0.016000	-1.2215e-06					
8								

	11 n-H20	12 mHCl	13 phi	14 LnaA	15 aA	16 xA	17 gA	18 mB^.5
0	0.54345	0.23165	0.96099	-0.0080208	0.99201	0.99172	1.00029	0.48130
1	0.55182	0.19034	0.95249	-0.0065322	0.99349	0.99319	1.00030	0.43628
2	0.55145	0.14239	0.94680	-0.0048575	0.99515	0.99490	1.00026	0.37735
3	0.55253	0.096753	0.93832	-0.0032710	0.99673	0.99653	1.00021	0.31105
4	0.55433	0.064977	0.93704	-0.0021937	0.99781	0.99766	1.00014	0.25491
5	0.55470	0.044001	0.91427	-0.0014494	0.99855	0.99842	1.00013	0.20976
6	0.55289	0.031939	0.91912	-0.0010577	0.99894	0.99885	1.00009	0.17872
7								