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

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

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

1. $a_A = \gamma_A\, x_A$ \hspace{2em} (activity coef. $\times$ mole fraction)

2. $x_A = n_A/(n_A + \nu\, n_B)$ \hspace{1em} (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

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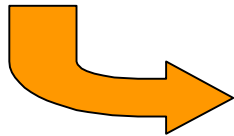
$$K_m = \frac{m'\,\alpha^2}{(1 - \alpha)'} = \frac{(m'-m)^2}{2m - m'}$$

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

#	T-t'st	t-corc	m-samp	v-tit	nB	mass-B	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					

	n-H2O	mHCl	phi	lnaA	aA	xA	gA	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								

Thermal Expansivity

A. Underpinning Purposes

1. Experience in using a *known* substance to calibrate a device, for subsequent application to an *unknown* substance.

2. Acquaintance with two simple devices — the *pycnometer* and the *dilatometer* — capable of giving very precise results for a fundamental physical property of liquid substances.

B. Theory

1. $\alpha \equiv \dfrac{1}{V}\left(\dfrac{\partial V}{\partial T}\right)_P = \left(\dfrac{\partial \ln V}{\partial T}\right)_P$ and, since $\rho = m/V$, $\alpha = -\left(\dfrac{\partial \ln \rho}{\partial T}\right)_P$

2. Integration $\Rightarrow$ $V = V_r \exp[\alpha(T - T_r)]$ where α is assumed to be independent of T near some reference $T = T_r$.

3. More general: If $f(T, T_r)$ is a function that $= 0$ when $T = T_r$, where $V = V_r$, then if V is expressed $V = V_r \exp[f(T, T_r)]$

   $$\alpha = df/dT$$

C. Experiment

1. Known is "standard mean ocean water." Its density is a function of T, so calibration requires measuring m and T.

2. Both this and the unknown (an alcohol) must be degassed beforehand to prevent air bubble formation.

3. Thermal equilibrium is *not* achieved instantly!

4. Data obtained in range 10-40°C; suffices to determine whether α is T-dependent over this range.

5. Etched scales on both devices are in cm and mm.

6. Minor complications:

    Buoyancy correction in pycnometry masses.
    Thermal expansivity of Pyrex not negligible.

7. Modified instructions:
    (1) Do dilatometry for just three T ranges: ~15, 25, 35°C
    (2) Get density (pycnometry) for at least 4 Ts in this range.

Today's Practice Quiz

1. Our treatment of the $I_2 + M \leftrightarrow I_2M$ reaction yielded a straight-line relationship permitting us to extract K and ε_x from an appropriate plot of "y" vs. "x." If this expression is written as $y = a + bx$, the equilibrium constant K is given by

   a. a/b b. b/a c. $a \times b$ d. $1/a$ e. none of these

2. For the following reaction, $K = 8.6 \times 10^{19}$ at 25°C and $K = 1.09 \times 10^{15}$ at 125°C:

   $$Cl_2(g) + F_2(g) \leftrightarrow 2ClF(g)$$
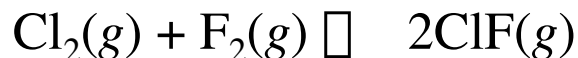
   Assuming that $\Delta H°$ and $\Delta S°$ are independent of T over this range, calculate $\Delta S°$.

   a. 3.7 J K^{-1} mol^{-1} b. 8.5 J K^{-1} mol^{-1} c. 11.3 J K^{-1} mol^{-1}
   d. −111.2 J K^{-1} mol^{-1} e. −113.7 J K^{-1} mol^{-1}

3. The reaction $A + B \leftrightarrow C$ is studied experimentally by mixing together solutions of A and B and determining concentrations at equilibrium. 10.0 mL of 0.036 m A is mixed with 5.0 mL of 0.126 m B, and at equilibrium [C] is found to be 0.0094 m. What is the value of K for this reaction?

   a. 2.1 L mol^{-1} b. 3.0 L mol^{-1} c. 9.3 L mol^{-1}
   d. 19.7 L mol^{-1} e. none of these