Activity (a) and Activity coefficient (γ)

- At moderate and high conc. of electrolyte soln.,the ions may associate as ion pairs (Na^+Cl^- | Na^+Cl^-) which the attraction force of appositely charge ion is small. or associate as ion triplets ($Na^+Cl^-Na^+$ | $Cl^-Na^+Cl^-$) with large attraction force.
- The electrostatic attraction and ion association minimized the collegative properties than expected for unhindered ions in the infinite dilution, so that the moderated and high conc.soln. having an effective conc. less than the actual or stoichiometric conc. It is called activity (a).

- a= M at infinite dilution or a/M=1
- But at moderate or high conc.
- $a/M = \gamma_{M,}$ $a/c = \gamma_{c,}$ $a/x = \gamma_{x}$
- γ:- activity coefficient, γ= 1 at infinite dilution

and usually↓ as the concentration↑.

- **Activity of electrolyte**

In electrolyte soln., each cation and anion have different activity

a_+ for cation, a_- for anion and $a_\pm$ for electrolyte

For example

$A_m B_n \rightarrow mA^+ + nB^-$, $a_{\pm} = (a_+^{m} * a_-^{n})^{1/(m+n)}$

$a_\pm$:- The mean ionic activity

For $NaCl \rightarrow Na^+ + Cl^-$ $a_{\pm} = (a_{Na}^{1} * a_{Cl}^{1})^{1/2}$

For $FeCl_3 \rightarrow Fe^{3+} + 3Cl^-$ $a_{\pm} = (a_{Fe}^{1} * a_{Cl}^{3})^{1/4}$

$a_{\pm} = \gamma_{\pm} [C_+^m * C_-^n]^{1/m+n}$ for any electrolyte

$C_+ = mC$, $C_- = nC$

For 0.01M FeCl3 $a_{\pm} = \gamma_{\pm} [C_+ * C_-^3]^{1/4}$

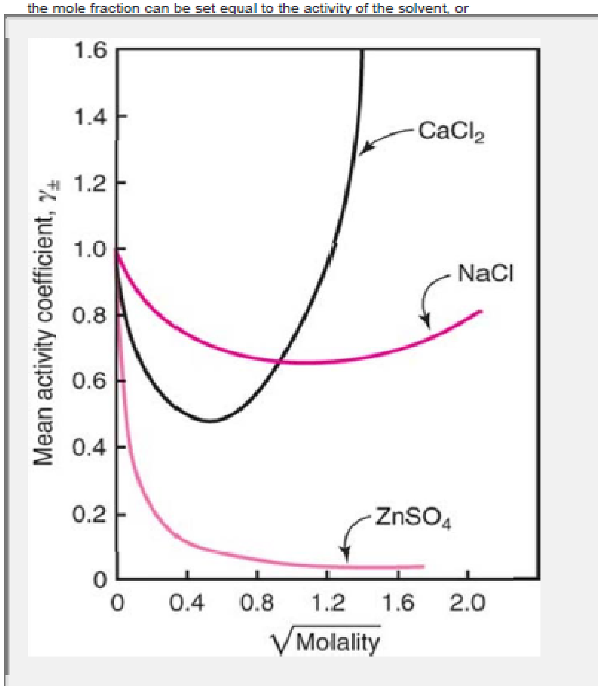
$a_{\pm} = \gamma_{\pm}[0.01 *(3X\ 0.01)^3]^{1/4} \quad = 2.3x10^{-2} \gamma_{\pm}$

Variation of $\gamma_{\pm}$ with concentration

1-initial ↓ in $\gamma_{\pm}$ with conc. is due to the interaction of ions

2- the minimum due to ion pair

3-the ↑ in curve due to ion triples in high conc.

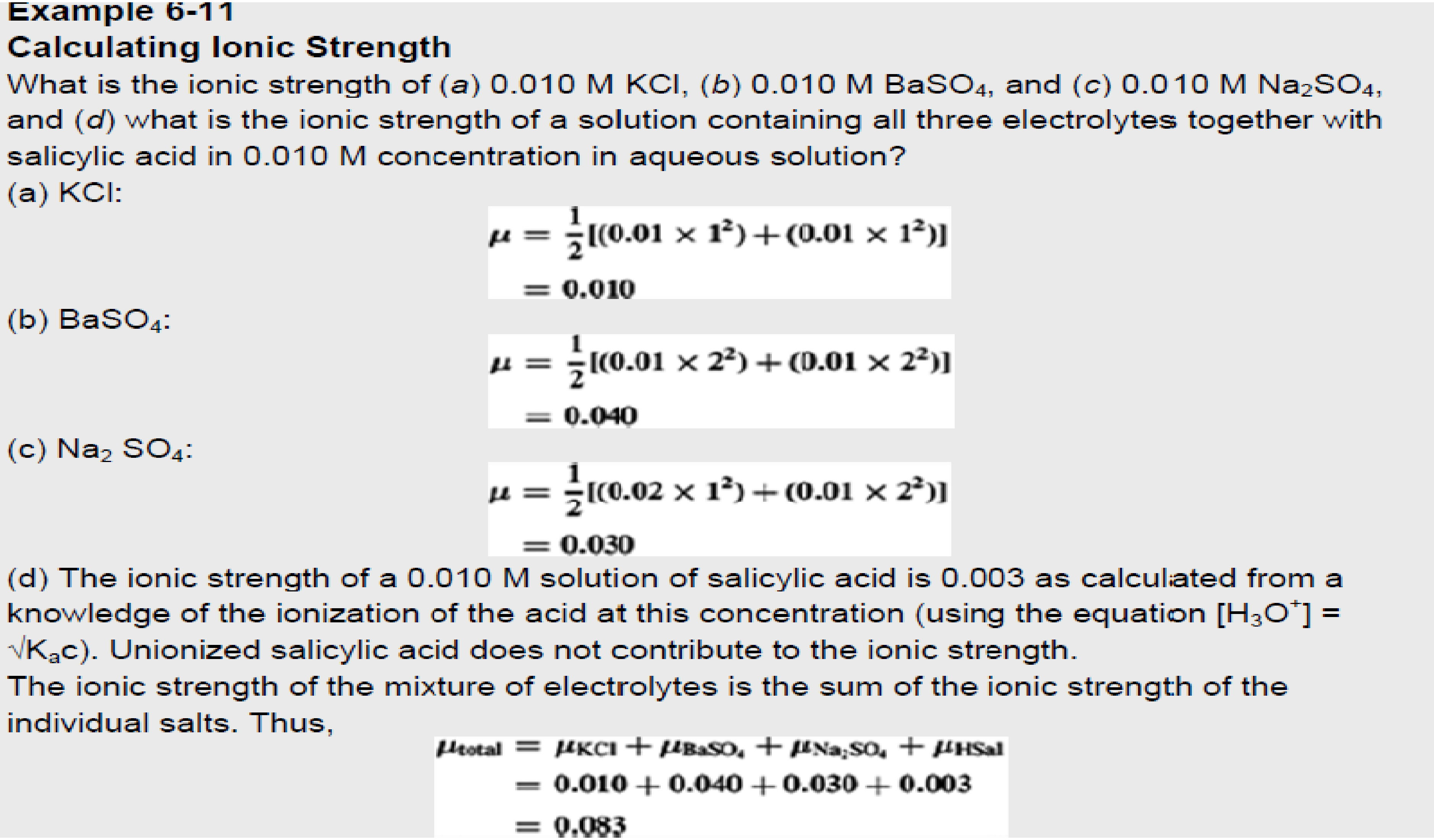


the mole fraction can be set equal to the activity of the solvent, or

Ionic strength (μ)

The ionic strength related to inter ionic attraction defined as:

$$\mu = ½ \sum_1^i C_i Z_i^2 = ½ [C_1 Z_1^2 + C_2 Z_2^2 + C_3 Z_3^2 + ... + C_n Z_n^2]$$



Example 6-11

Calculating Ionic Strength

What is the ionic strength of (*a*) 0.010 M KCl, (*b*) 0.010 M $BaSO_4$, and (*c*) 0.010 M Na_2SO_4, and (*d*) what is the ionic strength of a solution containing all three electrolytes together with salicylic acid in 0.010 M concentration in aqueous solution?

(a) KCl:

$$\mu = \frac{1}{2}[(0.01 \times 1^2) + (0.01 \times 1^2)] \\ = 0.010$$

(b) $BaSO_4$:

$$\mu = \frac{1}{2}[(0.01 \times 2^2) + (0.01 \times 2^2)] \\ = 0.040$$

(c) $Na_2 SO_4$:

$$\mu = \frac{1}{2}[(0.02 \times 1^2) + (0.01 \times 2^2)] \\ = 0.030$$

(d) The ionic strength of a 0.010 M solution of salicylic acid is 0.003 as calculated from a knowledge of the ionization of the acid at this concentration (using the equation $[H_3O^+] = \sqrt{K_a c}$). Unionized salicylic acid does not contribute to the ionic strength.

The ionic strength of the mixture of electrolytes is the sum of the ionic strength of the individual salts. Thus,

$$\mu_{total} = \mu_{KCl} + \mu_{BaSO_4} + \mu_{Na_2SO_4} + \mu_{HSal} \\ = 0.010 + 0.040 + 0.030 + 0.003 \\ = 0.083$$

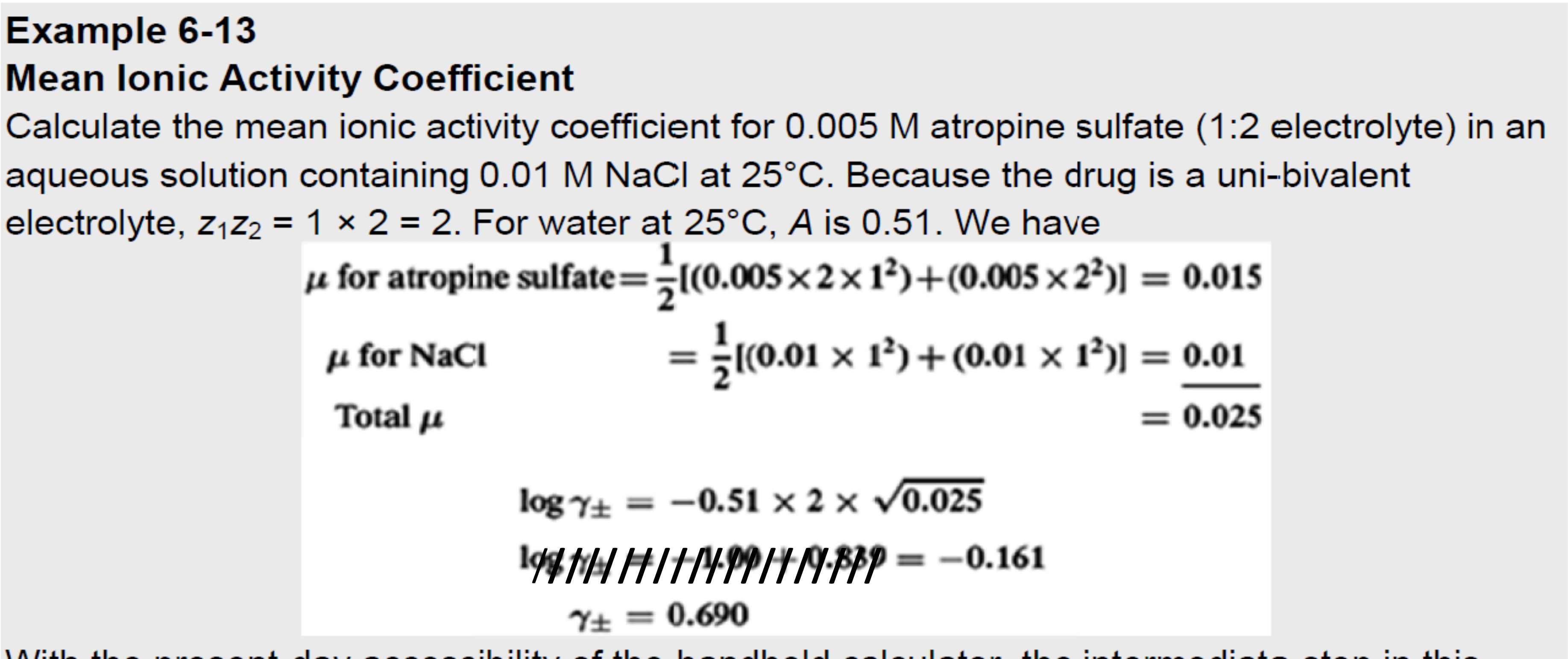
Calculation of mean ionic activity coefficient ($\gamma_\pm$)

$\log \gamma_\pm = - A Z_+ Z_- \sqrt{\mu}$ for dilute soln. until $\mu = 0.02$, $A = 0.51$ for aqueous soln,= at 25^0C

$\log \gamma_\pm = - A Z_+ Z_- \sqrt{\mu}/(1 + \sqrt{\mu})$ for moderate conc. soln. until $\mu = 0.1$

$\log \gamma_\pm = (- A Z_+ Z_- \sqrt{\mu}/[1 + a_i B_i \sqrt{\mu}]) + C$, C, B_i: constants values

a_i: ionic size parameter



Example 6-13

Mean Ionic Activity Coefficient

Calculate the mean ionic activity coefficient for 0.005 M atropine sulfate (1:2 electrolyte) in an aqueous solution containing 0.01 M NaCl at 25°C. Because the drug is a uni-bivalent electrolyte, $z_1 z_2 = 1 \times 2 = 2$. For water at 25°C, *A* is 0.51. We have

$$\mu \text{ for atropine sulfate} = \frac{1}{2}[(0.005 \times 2 \times 1^2) + (0.005 \times 2^2)] = 0.015$$

$$\mu \text{ for NaCl} = \frac{1}{2}[(0.01 \times 1^2) + (0.01 \times 1^2)] = 0.01$$

$$\text{Total } \mu = 0.025$$

$$\log \gamma_\pm = -0.51 \times 2 \times \sqrt{0.025}$$

$$\cancel{\log \gamma_\pm = -1.00 + 0.839} = -0.161$$

$$\gamma_\pm = 0.690$$

With the present-day accessibility of the handheld calculator, the intermediate step in this

Coefficient for expressing of Colligative properties

1- L coefficient or L value

The cryoscopic equation, $\Delta T_f = iK_f\ m$ **can be modified to**

$\Delta T_f = LC$ **where C is the molar concentration**

L value computed from experimental data, it is values with concentration. At isotonic concentration of drug with body L is designated Liso

so $\Delta T_f = iK_f\ m = \text{Liso}$ (

Some Liso values

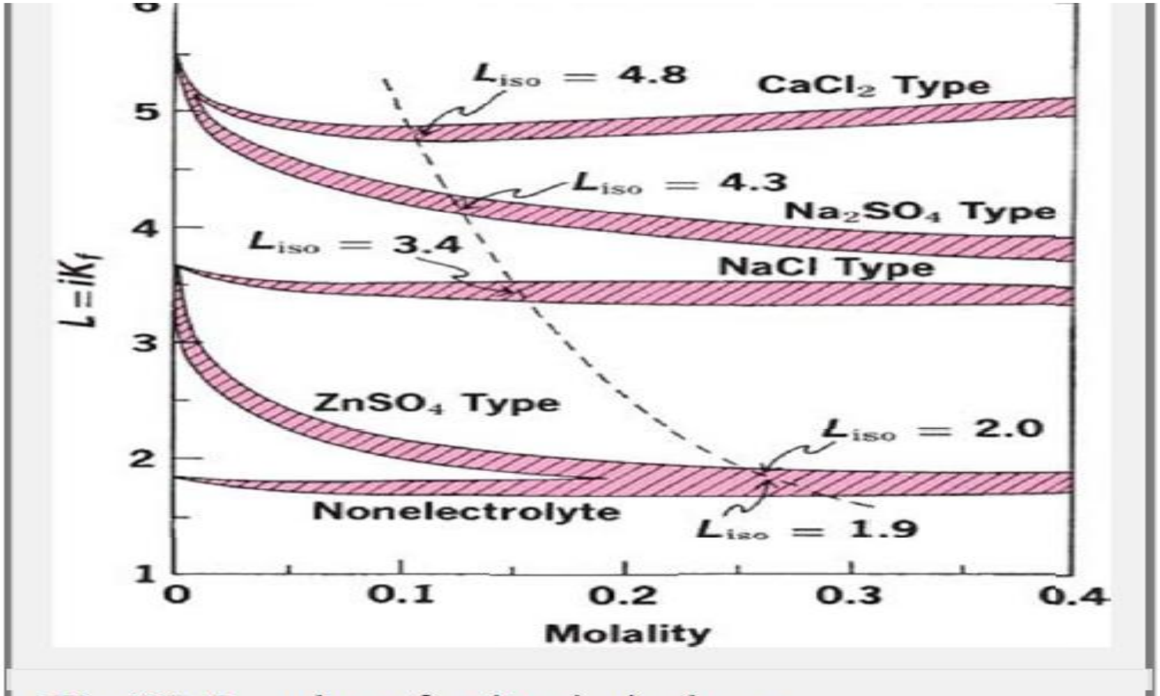


Fig. 6-7. L_{iso} values of various ionic classes.

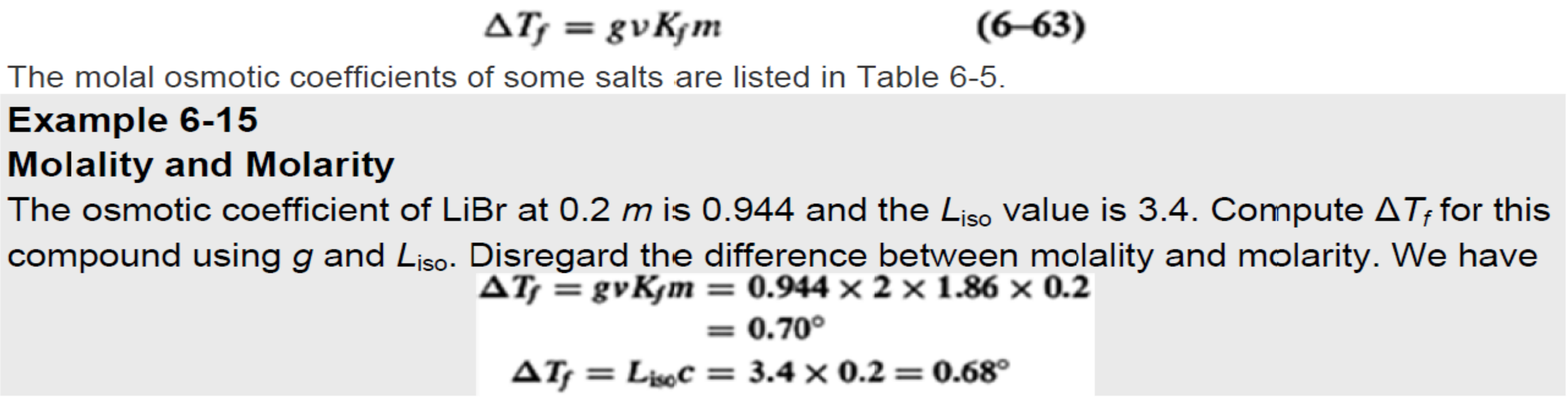
Osmotic coefficient (g)

Other methods for correcting deviations of ideality behavior from colligative properties is Osmotic coefficient (g).

At infinite dilution $i=\nu$ so $i/\nu=1$

The ratio i/ν designated as g (***practical osmotic coefficient***)so $i= g\nu$ and cryoscopic equation will be $\Delta T_f= g\nu K_f\, m$

$i= g\nu$, we have $\alpha=i-1/(\nu-1)$ we can calculate α from g and ν



$$\Delta T_f = g\nu K_f m \qquad (6\text{–}63)$$

The molal osmotic coefficients of some salts are listed in Table 6-5.

Example 6-15

Molality and Molarity

The osmotic coefficient of LiBr at 0.2 *m* is 0.944 and the L_{iso} value is 3.4. Compute ΔT_f for this compound using *g* and L_{iso}. Disregard the difference between molality and molarity. We have

$$\Delta T_f = g\nu K_f m = 0.944 \times 2 \times 1.86 \times 0.2$$
$$= 0.70°$$
$$\Delta T_f = L_{iso}c = 3.4 \times 0.2 = 0.68°$$