Answers Additional Tutorial A, Thermodynamics 2, 2025/2026

Exercise A1

a) We would normally write the enthalpy as a function of P and S, which gives the total differential

$$\mathrm{d}H = \left(\frac{\partial H}{\partial P}\right)_S \mathrm{d}P + \left(\frac{\partial H}{\partial S}\right)_P \mathrm{d}S, \quad \text{with} \quad \left(\frac{\partial H}{\partial P}\right)_S = V \quad \text{and} \quad \left(\frac{\partial H}{\partial S}\right)_P = T,$$

the latter equations following from the characteristic equation for the enthalpy: $\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}P$. Now we consider $H = H(P,T)$, which leads to the total differential

$$\mathrm{d}H = \left(\frac{\partial H}{\partial P}\right)_T \mathrm{d}P + \left(\frac{\partial H}{\partial T}\right)_P \mathrm{d}T.$$

If you find this peculiar, you might want to read appendix A of the study guide.

b) We take the partial derivative of the result of a) with respect to T at constant V:

$$\left(\frac{\partial H}{\partial T}\right)_V = \left(\frac{\partial H}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V + \left(\frac{\partial H}{\partial T}\right)_P.$$

N.B.: $\left(\frac{\partial H}{\partial P}\right)_T$ and $\left(\frac{\partial H}{\partial T}\right)_P$ are coefficients in the total differential of $H(P,T)$, and can therefore be considered as parameters when determining the derivative $\left(\frac{\partial H}{\partial T}\right)_V$.

c) First of all we recognize

$$\left(\frac{\partial H}{\partial T}\right)_P = C_P.$$

We use the following relations for exact differentials of state functions (Atkins: page 91-31 (ed. 9) or page 109 till 111 (ed. 10) or page 44 (ed. 11) or page 105 (ed. 12)):

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z} \quad \text{and}$$

$$\left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x,$$

implying

$$\left(\frac{\partial H}{\partial P}\right)_T = -\left(\frac{\partial H}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_H = -\mu C_P$$

and

$$\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P = -\frac{\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T} = \frac{V\alpha}{V\kappa_T} = \frac{\alpha}{\kappa_T}.$$

When we combine these results we find

$$\left(\frac{\partial H}{\partial T}\right)_V = \left(1 - \frac{\alpha\mu}{\kappa_T}\right) C_P.$$

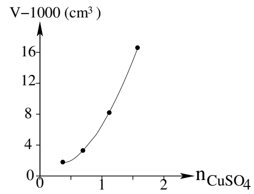
Exercise A2

a) Since the method is the same for all four cases, we only work it out for the first one (the values of the rest can be found in the table below).
The solution is 5 weight percent, so we have 5 g of $CuSO_4$ and 95 g water per 100 g.
We can use $\rho = \frac{M}{V}$ to determine the volume of the mixture. Per 1000 g water we have $\frac{5}{95}1000 =$ 52.6 g $CuSO_4$, so $M = 1052.6$ g
We therefore have a volume of $V = \frac{1052.6}{1.051} = 1001.55$ cm^3 per 1000 g water.

b) We can determine the amount of $CuSO_4$ using $n_{CuSO_4} = \frac{52.63}{159.6} = 0.3298$.

c) For the four solutions we find

n_{CuSO_4}	V (cm^3)
0.3298	1001.55
0.6962	1003.71
1.1057	1008.12
1.5664	1016.26



d) The partial molar volume of $CuSO_4$ still is a function of n_{CuSO_4} and is defined by $V_{CuSO_4} = \left(\frac{\partial V}{\partial n_{CuSO_4}}\right)_{n_{\text{water}}}$, so V_{CuSO_4} can be determined by differentiating V with respect to n: $\frac{\partial V}{\partial n} = b + 2.5cn^{1.5}$. The results can be found in the following table

n_{CuSO_4}	V_{CuSO_4} (cm^3/mol)
0.3298	4.05
0.6962	7.97
1.1057	13.8
1.5664	21.8

e) $V_{\text{water}} = \left(\frac{\partial V}{\partial n_{\text{water}}}\right)_{n_{CuSO_4}}$.
We could calculate V_{water} in a similar way (certain amount of $CuSO_4$ (e.g. 100 g), fit the graph of $V(n_{\text{water}})$, differentiate with respect to n_{water}).
It is however easier to use $V = V_{\text{water}} n_{\text{water}} + V_{CuSO_4} n_{CuSO_4}$. We determine the amount of mole n_{water} with $n_{\text{water}} = \frac{M_{\text{water}}}{m_{\text{water}}}$, so $n_{\text{water}} = \frac{1000}{18} = 55.56$ for all four solutions.
This results are shown in the following table

V(cm^3)	V_{CuSO_4} (cm^3/mol)	n_{CuSO_4}	n_{water}	V_{water} (cm^3/mol)
1001.55	4.05	0.3298	55.56	18.00
1003.71	7.97	0.6962	55.56	17.97
1008.12	13.8	1.1057	55.56	17.87
1016.26	21.8	1.5664	55.56	17.68

V_{water} should be 18 (cm^3/mol) for a very dilute solution. The first value in the table should therefore be smaller than 18 (cm^3/mol).

Exercise A3

a) We label the two compounds A and B. For an ideal mixture (a mixture in which there is no difference between the interactions between A and A, B and B or A and B), the total volume will simply be the sum of the two original volumes. So in terms of the molar volumes $V_{m,A}$ en $V_{m,B}$ we get

$$V = V_{ideal} = n_A V_{m,A} + n_B V_{m,B}, \quad \text{so} \quad V_A = \left(\frac{\partial V}{\partial n_A}\right)_{T,P,n_B} = V_{m,A} \quad \text{and} \quad V_B = V_{m,B}.$$

N.B., the partial molar volume $V_A = \left(\frac{\partial V}{\partial n_A}\right)_{T,P,n_B}$ is not to be confused with the molar volume $V_{m,A} = \frac{V^*}{n_A}$. The latter is defined on the basis of the volume V^* of the pure compound A.; only for an ideal solution $V_A = V_{m,A}$.

b)

$$V = V_{ideal} + V^E \quad \text{with} \quad V_{ideal} = n_A V_{m,A} + n_B V_{m,B}.$$

To calculate the partial molar volumes, we first need to translate the molar excess volume to an excess volume according to $V^E = nV_m^E = (n_A + n_B) V_m^E$. If we rewrite V^E in terms of n_A and n_B, we get

$$V^E = (n_A + n_B) V_m^E = (n_A + n_B) \frac{n_A n_B}{(n_A + n_B)^2} \left(a_0 + a_1 \frac{n_A - n_B}{n_A + n_B}\right) \quad \text{so}$$

$$V = n_A V_{m,A} + n_B V_{m,B} + \frac{n_A n_B}{n_A + n_B} \left(a_0 + a_1 \frac{n_A - n_B}{n_A + n_B}\right).$$

We can find the partial molar volume of propionic acid using

$$V_A = \left(\frac{\partial V}{\partial n_A}\right)_{T,P,n_B} = V_{m,A} + \frac{a_0 n_B^2}{(n_A + n_B)^2} + \frac{a_1 (3n_A - n_B) n_B^2}{(n_A + n_B)^3} = V_{m,A} + a_0 x_B^2 + a_1 (3x_A - x_B) x_B^2.$$

In the same way we find for V_B

$$V_B = V_{m,B} + a_0 x_A^2 + a_1 (x_A - 3x_B) x_A^2.$$

c) In an equimolar solution we have $x_A = x_B = 0.5$. The molar volumes can be calculated using

$$V_{m,A} = \frac{M_A}{\rho_A} = \frac{74.08 \text{ g/mol}}{0.97174 \text{ g/cm}^3} = 76.23 \text{ cm}^3\text{mol}^{-1} \quad \text{and} \quad V_{m,B} = \frac{86.13 \text{ g/mol}}{0.86398 \text{ g/cm}^3} = 99.69 \text{ cm}^3\text{mol}^{-1}.$$

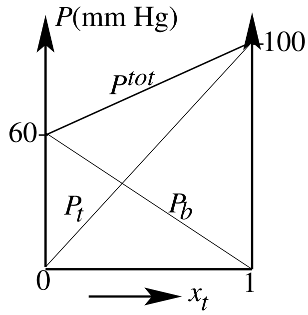
Using these values we obtain

$$V_A = 76.23 - 2.4697 \cdot 0.5^2 + 0.0608 \cdot (3 \cdot 0.5 - 0.5) \cdot 0.5^2 = 75.63 \text{ cm}^3\text{mol}^{-1} \quad \text{and} \quad V_B = 99.06 \text{ cm}^3\text{mol}^{-1}.$$

Exercise A4

Since toluene and benzene form an ideal solution, Raoult's law applies to the entire plot: $P_t = x_t P_t^*$ en $P_b = x_b P_b^*$, in which
P_i is the partial vapour pressure of component i,
$x_i = \frac{n_i}{n_t + n_b} = \frac{n_i}{n}$ the molar fraction of component i in the mixture and
P_i^* the vapour pressure i in case of a pure compound.

a) $P_t^* = 100$ mm Hg and $P_b^* = 60$ mm Hg at 27 °C, so the P, x-diagram becomes ($P^{tot} = P_t + P_b$):



b) We derived the Gibbs free energy of an ideal binary mixture to be

$$\Delta_{mix}G = n_t RT \ln x_t + n_b RT \ln x_b = nRT(x_t \ln x_t + x_b \ln x_b).$$

At 27 °C we have $x_t = \frac{6}{4+6} = 0.6$ and $x_b = \frac{4}{4+6} = 0.4$

$$\Delta_{mix}G = 6 \cdot 8.3 \cdot 300 \ln 0.6 + 4 \cdot 8.3 \cdot 300 \ln 0.4 = -17 \text{ kJ}.$$

The entropy of mixing is

$$\Delta_{mix}S = -\left(\frac{\partial \Delta_{mix}G}{\partial T}\right)_{P,n_t,n_b} = -nR(x_t \ln x_t + x_b \ln x_b) = -\frac{\Delta_{mix}G}{T} = -\frac{-17 \text{ kJ}}{300 \text{ K}} = 56 \text{ J/K}.$$

The enthalpy of mixing can be found using $\Delta G = \Delta H - T\Delta S$ at constant T, and therefore

$$\Delta_{mix}H = \Delta_{mix}G + T\Delta_{mix}S = -17 \text{ kJ} + 17 \text{ kJ} = 0 \text{ J}.$$

This is a direct consequence of the fact that we consider the mixture of benzene and toluene to be ideal. The enthalpy of mixing will generally not be zero for a real mixture.

c) According to Raoult's law $P_t = x_t P_t^* = 0.6 \cdot 100 = 60$ mm Hg and $P_b = x_b P_b^* = 0.4 \cdot 60 = 24$ mm Hg, so the mole fractions y_i in the vapour are $y_t = \frac{60}{60+24} = \frac{60}{84}$ and $y_b = \frac{24}{84}$.

Exercise A5

a) In figure 1 R indicates Raoult's law and H indicates Henry's law; subscripts are a(cetone) and c(hloroform).

b) For a mixture of 99 mol acetone and 1 mol chloroform the majority comopnent is acetone.
For acetone therefore Raoult's law ia applicable and for chloroform Henry's law, so
$P_a = x_a P_a^* = \frac{99}{99+1} 300 = 297$ mm Hg and
$P_c = x_c K_c = \frac{1}{99+1} 166 = 1.66$ mm Hg.
ΔG is $\Delta_{mix}G = G_f - G_i = G - G_i$.
Initially: $G_i = n_a \mu_a^* + n_c \mu_c^*$, where $\mu_{a,c}^* = \mu_{a,c}^\ominus + RT \ln \frac{P_{a,c}^*}{P_{a,c}^\ominus}$.
Once mixed we find $G = n_a \mu_a + n_c \mu_c$, where $\mu_{a,c} = \mu_{a,c}^\ominus + RT \ln \frac{P_{a,c}}{P_{a,c}^\ominus}$, so
$\Delta_{mix}G = n_a RT \ln \frac{P_a}{P_a^*} + n_c RT \ln \frac{P_c}{P_c^*}$, and therefore
$\Delta_{mix}G = 99 \cdot 8.31 \cdot 300 \ln \frac{297}{300} + 1 \cdot 8.31 \cdot 300 \ln \frac{1.66}{200} = (-2.48 - 11.9) \cdot 10^3 = -14.4$ kJ.

c) $\Delta_{mix}S = -\left(\frac{\partial \Delta_{mix}G}{\partial T}\right)_{P,n_a,n_c} = -\frac{\Delta_{mix}G}{T} = \frac{14.4 \cdot 10^3}{300} = 48$ J/K.
$\Delta_{mix}H = \Delta_{mix}G + T\Delta_{mix}S = -14.4 \cdot 10^3 + 300 \cdot 48 = 0$ J.
Note that despite the apparently zero $\Delta_{mix}H$ for the Henry-law, in reality this value is nonzero, because Henry's law is simply a linear approximation ($P_i \approx x_i K_i$) of the vapour pressure for small

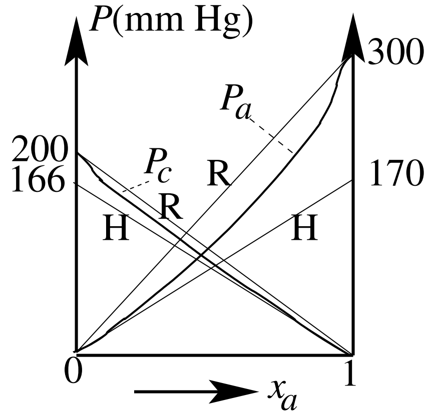


Figure 1:

mole fractions of the minority component i. With this approximation the behaviour seems to be Raoult-like.

d) See part b):
$P_a = x_a P_a^* = 297$ mm Hg and
$P_c = x_c K_c = 1.66$ mm Hg.
The vapour composition is therefore given by $y_a = \frac{297}{297+1.66} = 0.994$ and $y_c = 1 - 0.994 = 0.006$.

Exercise A6

a) $X^E = \Delta_{mix}X - \Delta_{mix}X^{ideal}$. For an ideal solution Raoult's law gives
$\Delta_{mix}G^{ideal} = nRT(x_1 \ln x_1 + x_2 \ln x_2)$, so $G^E = \Delta_{mix}G - nRT(x_1 \ln x_1 + x_2 \ln x_2)$.
$\Delta_{mix}S^{ideal} = -nR(x_1 \ln x_1 + x_2 \ln x_2)$, so $S^E = \Delta_{mix}S + nR(x_1 \ln x_1 + x_2 \ln x_2)$.
$\Delta_{mix}H^{ideal} = 0$, and $H^E = \Delta_{mix}H$.

b) In the expression for G^E we do not see a symbol for the number of moles n, altough we are used to interpret G^E as an extensive (excess) Gibbs free energy, for which the units are $[G^E] = \text{J}$. Furthermore $[R] = \text{J/molK}$, $[T] = \text{K}$ and x is a fraction without units, such that $[g] = \text{mol}$.
The extensive excess-Gibbs free energy therefore is $G^E = ng'RTx(1-x)$, where $g' = g/n$ is without units.
The function is symmetrical in $x = 0.5$, so we can express x either as x_1 or x_2; we choose x_1.

c) $\mu_1 = \left(\frac{\partial G}{\partial n_1}\right)_{P,T,n_2}$ and analogously for μ_2. We are working at constant pressure and temperature and with that knowledge we can suppress the subscripts P, T resulting in $\mu_1 = \left(\frac{\partial G}{\partial n_1}\right)_{n_2}$.
$G^E = \Delta_{mix}G - \Delta_{mix}G^{ideal}$ and $\Delta_{mix}G = G_{f(inal)} - G_{i(nitial)}$.
For an extensive G^E we write nG^E according to part b), so
$\mu_1 = \left(\frac{\partial G}{\partial n_1}\right)_{n_2} = \left(\frac{\partial G_f^{ideal}}{\partial n_1}\right)_{n_2} + \left(\frac{\partial G^E}{\partial n_1}\right)_{n_2}$, or
$\mu_i = \mu_i^{ideal} + \mu_i^E$.
For an ideal solution Raoult's law holds ($P_1 = x_1 P_1^*$), such that
$\left(\frac{\partial G_f^{ideal}}{\partial n_1}\right)_{n_2} = \mu_1^{ideal} = \mu_1^* + RT \ln \frac{P_1}{P_1^*} = \mu_1^* + RT \ln x_1$.
For the excess-term we find (use $n = n_1 + n_2$ and $x_1 = n_1/(n_1 + n_2)$)
$\mu_1^E = \left(\frac{\partial G^E}{\partial n_1}\right)_{n_2} = \left(\frac{\partial ng'RTx_1(1-x_1)}{\partial n_1}\right)_{n_2} = \left(\frac{\partial n}{\partial n_1}\right)_{n_2} g'RTx_1(1-x_1) + ng'RT\left(\frac{\partial x_1(1-x_1)}{\partial n_1}\right)_{n_2} =$

$g'RTx_1(1-x_1) + ng'RT\left(\frac{\partial x_1(1-x_1)}{\partial x_1}\right)_{n_2}\left(\frac{\partial x_1}{\partial n_1}\right)_{n_2} = g'RTx_1(1-x_1) + ng'RT(1-2x_1)\frac{x_2}{n} = g'RTx_2^2.$
For μ_1 we obtain
$\mu_1 = \mu_1^* + RT\ln x_1 + g'RTx_2^2.$
For μ_2 we find an analogous expression. Because G^E is symmetrical in x_1 and x_2 ($G^E = g'RT(1-x_2)x_2 = g'RTx_2(1-x_2)$) and the same holds for $n = n_1 + n_2$, we find
$\mu_2 = \mu_2^* + RT\ln x_2 + g'RTx_1^2.$

d) The activity a_i of component i in the mixture is defined by $\mu_i = \mu_1^* + RT\ln a_i$, while the activity coefficient γ_i (on the mole fraction scale) of component i is defined by $a_i = \gamma_i x_i$.
Using the result of the former part we find $a_1 = x_1\exp\left(g'x_2^2\right)$, and so $\gamma_1 = \exp\left(g'x_2^2\right)$, while $a_2 = x_2\exp\left(g'x_1^2\right)$, and therefore $\gamma_2 = \exp\left(g'x_1^2\right)$.

e) μ_1 en μ_2 are easily plotted as function of x_1 (or x_2), using $x_1 = 1 - x_2$. If we choose $g = 0.01n$, $\mu^* = -1$ kJ/mol for both components and $T = 273$ K, the we find the result of Figure 2, in which the lower three curves represent the ideal solution case ($g = 0$). In the figure μ_1, μ_2 and $x_1\mu_1 + x_2\mu_2$ are plotted. For the same situation but with $\mu_1^* = -1$ kJ/mol and $\mu_2^* = -2$ kJ/mol we find the

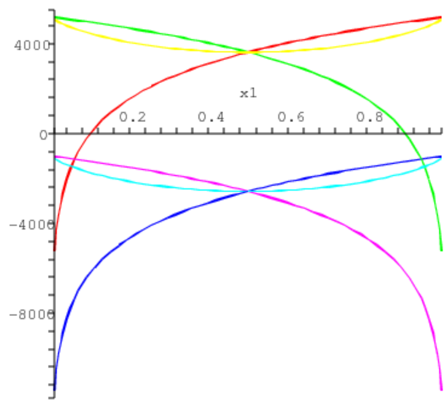


Figure 2: μ_1 and μ_2 as a function of x_1, for $\mu^* = -1$ kJ/mol for both components and $T = 273$ K; $g = 0.01n$ for the upper three curves and $g = 0$ for the lower curves.

result in figuur 3.

f) Compare the result of exercise 17d. $\Delta_{mix}G = \Delta_{mix}H - T\Delta_{mix}S$. If g is independent of T then we interpret $G^E = gRTx_1x_2$ as an excess entropy, such that $\Delta_{mix}S = -nR(x_1\ln x_1 + x_2\ln x_2 + g'x_1x_2)$ and $\Delta_{mix}H = 0$.

g) $\Delta_{mix}H = 0$ suggests that the solution behaves as ideal. This is however not the case because $S^E = -gRx(1-x) \neq 0$ and therefore we are dealing with an athermal mixture (cf. once more exercise 17d).

Exercise A7

We calculate the freezing point using the data $T^*_{\mathrm{H_2O}} = 273.15$ K; $\Delta_{fus}H_{\mathrm{H_2O}} = 6.008$ kJ/mol; $M_{\mathrm{sucrose}} = 342.30$ g/mol; $M_{\mathrm{H_2O}} = 18.015$ g/mol and $\rho_{\mathrm{H_2O}} = 0.997$ g/cm^{-3}. M and ρ are specified at 298 K and 293 K, respectively. The error due to the temperature difference we can neglect, in particular because

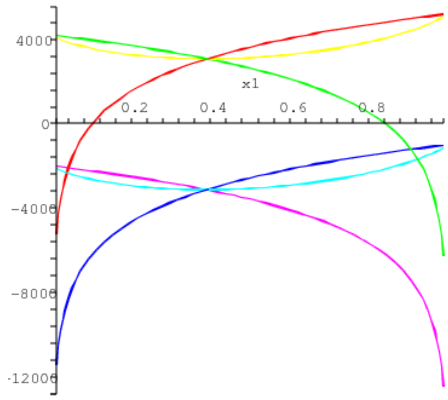


Figure 3: Same plot for $\mu_1^* = -1$ kJ/mol and $\mu_2^* = -2$ kJ/mol.

the expression we use for the freezing point depression already has quite some approximations in its derivation.

$$\Delta T = K x_B, \quad \text{where} \quad K = \frac{RT^{*2}}{\Delta_{fus}H} \quad \text{so} \quad \Delta T = \frac{8.314 \cdot 273.15^2}{6.008 \cdot 10^3} \frac{\frac{7.5}{342.30}}{\frac{7.5}{342.30} + \frac{0.997 \cdot 250}{18.015}} = 0.161 \text{ K}.$$

Exercise A8

We can calculate the freezing point depression using $\Delta T = K x_B$ in which $K = \frac{RT^{*2}}{\Delta_{fus}H}$. We use the values $T^*_{H_2O} = 273.15$ K; $\Delta_{fus}H_{H_2O} = 6.008$ kJ/mol; $M_{H_2O} = 18.015$ g/mol and $\rho_{H_2O} = 0.997$ g/cm^{-3}, resulting in $K = \frac{8.314 \cdot 273.15^2}{6.008 \cdot 10^3} = 103.2$ K. For a melting point depression of $\Delta T = 1$ °C we need a mole fraction of solute of $x_B = \frac{\Delta T}{K} = \frac{1}{103.2} = 9.7 \cdot 10^{-3}$. $x_B = \frac{n_B}{n_A + n_B} \approx \frac{n_B}{n_A}$. The necessary amount of grams is therefore $m_B = n_B M_B \approx x_B n_A M_B = x_B \frac{m_A}{M_A} M_B$. So for 1 L $\approx 10^3$ g water we need $m_B \approx 9.7 \cdot 10^{-3} \frac{10^3}{18.015} M_B = 0.54 M_B$ (g).

a) $M_{\text{DMSO}} = 78.13$ g/mol, so the necessary amount is $m_{\text{DMSO}} \approx 42$ g.

b) $M_{\text{sucrose}} = 342.30$ g/mol, so the necessary amount is $m_{\text{sucrose}} \approx 184$ g. This seems a lot, but the solubility is 2115 g/L at 20 °C, so it will work just fine.

c) In this case we have two complications. First of all, we increase the amount of water by adding the the hydrochloric acid (hopefully negligible for an estimate). Secondly, we have a factor 1/2 in x_B because the strong acid fully dissociates into two ions. To start of we neglect the increase of the amount of water: $M_{\text{HCl}} = 36.5$ g/mol, so $m_{\text{HCl}} \approx \frac{1}{2} \cdot 0.54 \cdot 36.5 = 9.8$ g, which corresponds to about 0.27 L hydrochloric acid. That is not quite negligible compared to 1 L and therefore an underestimation.
We repeat the calculation without the assumption. Each mol ions corresponds to 0.5 mol HCl and therefore 0.5 L added hydrochloric acid, which is about 28 mol water. So we have to replace $x_B = \frac{n_B}{n_A + n_B}$ by $x_B = \frac{n_B}{n_A + 28 n_B + n_B}$. Using $\Delta T = K x_B$ we find $n_B = \frac{n_A}{\frac{K}{\Delta T} - 29} = \frac{\frac{10^3}{18.015}}{103.2 - 29} = 0.75$ mol, so 0.37 L hydrochloric acid (about 370 g).