PP 14.1

hexane (1) + furfural (2)

①

$$\ln \gamma_i = x_j^2 \left(\frac{800}{T(°K)}\right)$$

96 g/mole
BP 323 °F (162°C)

Follow Pg 546 + Example 14.4

$x_1^\alpha \; x_2^\alpha \; x_1^\beta \; x_2^\beta$

298°K

$A_{12} = 900/298 = 2.68$

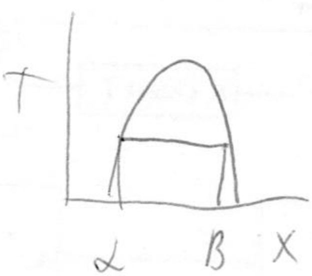
$$\frac{G^E}{RT} = A_{12} x_1 x_2$$

$$\frac{\Delta G^{ig}_{mix}}{RT} = \sum x_i \ln x_i$$

$$\ln \gamma_1^\alpha = \ln \gamma_2^\alpha = 2.68\, x_2^2 = 2.68\, x_1^2$$

$x_1 = x_2$

$$\frac{\Delta G_{mix}}{RT} = \frac{G^E}{RT} + \frac{\Delta G_{ig}}{RT}$$



$$x_1^\alpha = x_2^\beta = \frac{1}{\exp(2.68)} = 0.069$$

symmetry of A_{12}

$x_{1\beta} = 1 - 0.069 = 0.931$

$$\gamma_i^\alpha x_i^\alpha = \gamma_i^\beta x_i^\beta$$

$$K_1 = \frac{x_1^\alpha}{x_1^\beta} = \frac{\gamma_1^\beta}{\gamma_1^\alpha}$$

$$x_1^\beta = \frac{1 - K_2}{K_1 - K_2} \qquad x_1^\alpha = x_1^\beta K_1$$

$$K_1 = \frac{0.069}{0.931} = 0.074$$

$$K_2 = \frac{(1-0.069)}{(1-0.931)} = 13.58$$

$$x_1^\beta = \frac{1 - 13.58}{0.074 - 13.58} = 0.931$$

$x_1^\alpha = 0.0689$

$$x_1^{\alpha} = x_2^{B} = \frac{1}{\exp(2.68)} = 0.069$$

$x_2^{\alpha} = 0.931$ $x_1^{B} = 0.931$

$$\gamma_1^{\alpha} = \exp\left((x_2^{\alpha})^2\, 2.68\right) = 10.20$$

$$\gamma_2^{\alpha} = \exp\left((x_1^{\alpha})^2\, 2.68\right) = 1.01$$

$$\gamma_1^{B} = \exp\left((x_2^{B})^2\, 2.68\right) = 1.01$$

$$\gamma_2^{B} = \exp\left((x_1^{B})^2\, 2.68\right) = 10.20$$

$$K_1 = \frac{\gamma_1^{B}}{\gamma_1^{\alpha}} = \frac{1.01}{10.20} = 0.099 \qquad K_2 = \frac{\gamma_2^{B}}{\gamma_2^{\alpha}} = 10.076$$

(3) $$x_{1\,new}^{B} = \frac{1 - K_{2\,old}}{K_{1\,old} - K_{2\,old}} = 0.851$$

$$x_{2\,new}^{B} = 0.149$$

(4) $$x_{1\,new}^{\alpha} = x_{1\,new}^{B} K_{1\,old} = 0.084$$

$$x_{2\,new}^{\alpha} = 0.916$$

(5) $$\gamma_1^{\alpha} = \exp\left((x_{2\,new}^{\alpha 2})\, 2.68\right) = 9.464$$

$$\gamma_2^{\alpha} = \exp\left((x_{1\,new}^{\alpha 2})\, 2.68\right) = 1.019$$

$$\gamma_1^{B} = \exp\left(x_2^{B2}\, 2.68\right) = 1.061$$

$$\gamma_2^{B} = \exp\left((x_1^{B})^2\, 2.68\right) = 6.965$$

(2) $K_1 = \frac{\gamma_1^\beta}{\gamma_1^\alpha} = \frac{1.061}{9.464} = 0.1121$

$K_2 = \frac{\gamma_2^\beta}{\gamma_2^\alpha} = \frac{6.965}{1.019} = 6.835$

(3) $x_1^\beta = \frac{1-K_2}{K_1-K_2} = 0.8679$

$x_2^\beta = 1 - x_1^\beta = 0.1321$

$x_1^\alpha = x_1^\beta K_1 = 0.0973$ → going to about 10%

$x_2^\alpha = 0.9027$

Pr. 14.2

H_2O (1)

(2)

α | β

ρ 0.866 g/cc
BP 136 °C
MW = 106 g/mol
C8H10

$x_1^\beta = 0.01$ $x_2^\beta = 0.99$

Find

$x_2^\alpha = ?$ UNIFAC $\frac{\Delta G^E}{RT} = 0.0077$

$$K_2 = \frac{x_2^\alpha}{x_2^\beta} = \frac{x_2^\alpha}{0.99} = \frac{0.04 - 0.0077}{0.09}$$

1.0000 − .9979 18 g/mol = 17.96 g
.0100

.002 106 g/mol = 0.223 g

mole %

0.012 wt%

use

14.03
example M

ACH	0	5
AC CH2	0	1
CH3	0	1
H2O	1	0

PP 19.3

(1) water + (2) isobutanol

↓

$z_{H_2O} = 0.6719$ (1)

89.92 °C

1 atm

Analyzed

$A_{12}^{VL} = 1.566 \quad A_{21} = 3.833$ @ 273 °K

Van Laar Model

$x_1^{\alpha} = ?$

$x_1^{\beta} = ?$

component fugacity

$a_i = \frac{f_i}{f_i^{\circ}} = x_i \gamma_i = 1$ for pure

$a_1^{\alpha} = a_1^{\beta}$ & $a_2^{\alpha} = a_2^{\beta}$ def

P. 470

$$\ln \gamma_1 = \frac{A_{12}}{\left[1 + \frac{A_{12} x_1}{A_{21} x_2}\right]^2}$$

$$\ln \gamma_2 = \frac{A_{21}}{\left[1 + \frac{A_{21} x_2}{A_{12} x_1}\right]^2}$$

$$\gamma_1^{\alpha} x_1^{\alpha} = \gamma_1^{\beta} x_1^{\beta}$$

$$\frac{\gamma_1^{\alpha}}{\gamma_1^{\beta}} = \frac{x_1^{\beta}}{x_1^{\alpha}}$$

$\frac{\Delta G_{mix}}{RT}$

$$\frac{\Delta G^E}{RT} = \frac{A_{12} A_{21} x_1 x_2}{(x_1 A_{12} + x_2 A_{21})}$$

+

$$\frac{\Delta G}{RT}(IS) = x_1 \ln x_1 + x_2 \ln x_2$$

PP 14.4

SSCED (1)

I_2 (2) CCl_4 298 K

T_m = 387 K
ΔH^f = 15.5 kJ/mol

SLVE
$(x_1)_L$

Example 14.8 p. 560

g/mol   Assume ideal soln

$$x_{I_2} = \exp\left[\left(\frac{-\Delta H^f}{R}\right)\left(\frac{1}{T} - \frac{1}{T_m}\right)\right]$$

ρ g/cm³

$x_{mole} \cdot \frac{MW\ g/mol}{\rho\ g/cc}$

$$= \exp\left(\left(-\frac{15500\ J/mol}{8.314\ J/mol\,K}\right)\left(\frac{1}{298\,K} - \frac{1}{387\,K}\right)\right)$$

$$= 0.237$$

p. 482
SSCED

$\lambda = \delta = 17.5\ \frac{J}{cm^3}$ — I_2

$\tau = 0$?

$\alpha = 1.25$
$\beta = 0.64$

Need
α
β for I_2
δ ?

$$\Phi = \frac{0.237\left(\frac{MW}{\rho}\right)_{I_2}}{0.237\left(\frac{MW}{\rho}\right)_{I_2} + 0.763\left(\frac{MW}{\rho}\right)_{CCl_4}} = 0.076$$

$25.7\left(\frac{126.9\ g/mol}{4.933\ g/cm^3}\right)$ $\left(\frac{153.6}{1.58}\right)$ 97.2

$$(\delta_i')^2 = \delta_i^2 - 2\alpha_i\beta_i$$

p. 402 $$K_{12} = \frac{(\alpha_2-\alpha_1)(\beta_2-\beta_1)}{4\,\delta_2'\delta_1'}$$

$$RT\ln\gamma_K = V_K\,(1-\Phi_K)^2\Big[\left[\delta_2'-\delta_1'\right]^2 + 2K_{12}\,\delta_2'\delta_1'\Big]$$

fit γ_2

$$x_{2} = \frac{x_{\text{ideal}}}{\gamma_2}$$

then calc Φ_K ; γ_2 ; x_2

until it doesn't change

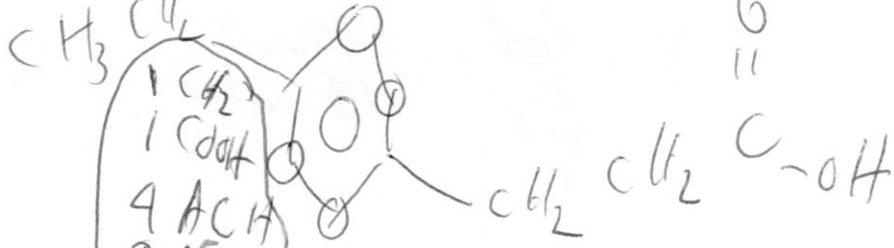
HW

8

(14.3)

2+3

$T = 37°C = 310°K$



1 CH_2
1 COOH
4 ACH
2 ACH_2
1 CH_3

$+ H_2O$
+
n octanol

$CH_3(CH_2)_7OH$

CH_3	1
CH_2	7
OH	1

(14.4) → $K_1 = \frac{x_1^{\alpha}}{x_1^{\beta}} = \frac{\gamma_1^{\beta}}{\gamma_1^{\alpha}}$

LLE
P. 564
Example 14.11
P. 486 12.75

$\gamma_1^{\infty} = \exp$

	octanol	drug
x =	0.8889	0.1111
γ =	1.0024	1.1422

	water	drug
x =	0.8889	0.1111
γ =	1.3207	27.0124

14.4 (9)

Assume

$x_1 = 1e{-3}$ ~ infinite dilute

~~$x_1 \ln \gamma_1^{\infty} = \frac{-\Delta H_f}{R}\left(\frac{1}{T} - \frac{1}{T_m}\right)$~~

UNIFAC Drug

$\gamma_1^{\infty\alpha} = 1.001 \quad \gamma_2^{\infty\alpha} = 12366.$ water

$\gamma_1^{\infty\beta} = 1.000 \quad \gamma_2^{\infty\beta} = 1.1889$ octanol

at 37°C $K = \frac{12,368}{1.1889} = 10,401$

$\gamma_1^{\alpha} x_1^{\alpha} = \gamma^{\beta} x_1^{\beta}$

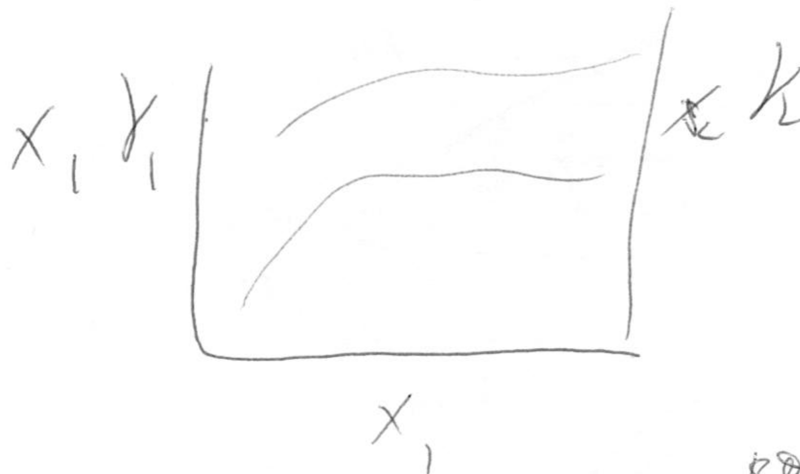
$\frac{x_1^{\alpha}}{x_1^{\beta}} = \frac{\gamma_1^{\beta}}{\gamma_1^{\alpha}} = 10,401$ goes to water

$\frac{x_1^{\alpha}}{x_1^{\beta}} = \frac{\gamma_1^{\beta}}{\gamma_1^{\alpha}} = \frac{1.1889}{1.000} = 1.1889$ octanol

HW 14.4

$$RT\ln\gamma_1 = V_1\Phi_2^2(\delta_1-\delta_2)^2$$

$$RT\ln\gamma_2 = V_2\Phi_1^2(\delta_1-\delta_2)^2$$



ΔG_{mix}

$$G_E = \Phi_1\Phi_2(\delta_1-\delta_2)^2(x_1V_1+x_2V_2)$$

$$+G^{id} = x_1\ln x_1 + x_2\ln x_2$$

X

Set up Excel & Calc.

	V (cm³/mole)	δ (cal/cm³)$^{1/2}$
heptane	122	6.2
CCl_2H_2	64	9.7

$$\Phi_1 = \frac{x_1V_1}{x_1V_1+x_2V_2} \qquad \Phi_2 = \frac{x_2V_2}{(x_1V_1+x_2V_2)}$$

(14.7) (1) methanol (2) cyclohexane

α
meth
ol

(a) $A_{12}^{m.ass} = \frac{(\alpha_2 - \alpha_1)(B_2 - B_1)(V_1 + V_2)}{4RT}$

	α	B	V_L cm³/mole
Methanol	17.43	14.99	40.1
Cyclohexane	0	0	109.1

(B) Page 546 target comp a plot

$(CH_2)_6$
12
6
72
12

$\frac{0.77 \ g/cc}{84 \ g/mole} \Rightarrow 109.1 \ cm^3/mol$

$\ln \gamma_1 = A_{12} x_2^2$
$\ln \gamma_2 = A_{12} x_1^2$

$x_1^{\alpha} \gamma_1^{\alpha} = x_1^{\beta} \gamma_1^{\beta}$

T = 298

(A) G_{mix}

SSCED

$$RT \ln \gamma_k = V_k (1-\Phi_k)^2 \left[(\delta_2' - \delta_1')^2 + 2 k_{12} \delta_2' \delta_1' \right]$$

$$(\delta_i')^2 = \delta_i^2 - 2\alpha_i \beta_i$$

$$k_{12} = \frac{(\alpha_2 - \alpha_1)(\beta_2 - \beta_1)}{4 \delta_2' \delta_1'}$$

UNIFAC use Excel Sheet

P. 548 $x_1^\alpha \gamma_1^\alpha = x_1^\beta \gamma_1^\beta = 1$ pure (13)

① Assume B is pure 1

$x_1^\alpha = 1/\gamma_1^{\alpha\infty}$

porephne "a = 1"

α is pure 2

$x_2^\beta = 1/\gamma_2^{\beta,\infty}$ $\gamma_2^{\beta,\infty}$ assume $x_{2\alpha} = 0.001$

② $K_{1,old} = \frac{\gamma_1^\beta}{\gamma_1^\alpha}$ $K_{2old} = \frac{\gamma_2^\beta}{\gamma_2^\alpha}$

③ $x_{1new}^\beta = \frac{(1-K_{2old})}{(K_{1old}-K_{2old})}$ $x_{2new}^\beta = 1 - x_{1new}^\beta$

④ $x_{1,new}^\alpha = K_{1old} x_{1new}^\beta$ $x_{2new}^\alpha = 1 - x_{1new}^\alpha$

⑤ ~~$x_1^\alpha \gamma_{1new}^\alpha = x_1^\beta \gamma_{1new}^\beta$~~

Use SSCED UNIFAC MAB to get γ_{1new}^α γ_{1n}^β from x's γ_{2n}^α γ_{2n}^β

⑥ Like 2 $K_{1new} = \frac{\gamma_{1new}^\beta}{\gamma_{1n}^\alpha}$

⑦ Go to ③ Loop until converge

(14.11)

water (1) / MEK (2)

299.85 K

$x_1^{\alpha} = 0.927$

$x_1^{\beta} = 0.364$

Example 14.9 p. 547

UNIQUAC

$r = [0.92, 3.2479]$

$q = [1.40, 2.876]$

$a_{12} = -2.0882$

$a_{21} = 345.534$

α water rich

β MEK rich

predict $\begin{pmatrix} x_1^{\alpha} \\ x_1^{\beta} \end{pmatrix}$

Use Actcoeff.xlsx

UNIQUACS

1) assume More α pure (1)

$x_1 = 0.999$ $x_2 = 0.001$

$\gamma_1^{\alpha\infty} = 1.000007$

$x_1^{\alpha} = \frac{1}{\gamma_1^{\alpha\infty}} = 0.999993$ $x_2^{\alpha} = 0.000007$

$\gamma_2^{\beta} = 1.000002$

$x_2^{\beta} = 0.999998$ $x_1^{\beta} = 0.000002$

2) $K_{1old} = \frac{\gamma_1^{\beta}}{\gamma_1^{\alpha}} = 6.90$

	α	β
γ_1	1	~~6.8998~~ 250.200
γ_2	25.288	1

$K_{2old} = \frac{\gamma_2^{\beta}}{\gamma_2^{\alpha}} = 0.0395$

3) $x_{1new}^{\beta} = \frac{(1 - K_{2old})}{(K_{1old} - K_{2old})} = 0.140$ $x_{2new}^{\beta} = 0.860$

4) $x_{1new}^{\alpha} = K_{1old} x_{1new}^{\beta} = 0.966$ $x_{2new}^{\alpha} = 0.034$

5) UNIQUAC → x_1

	α	β
γ_1	1.007	4.62
γ_2	16.36	1.03

6) $K_{1new} = \frac{\gamma_1^\beta}{\gamma_1^\alpha} = \frac{4.62}{1.007} = 4.59$

$K_{2new} = \frac{\gamma_2^\beta}{\gamma_2^\alpha} = \frac{1.03}{16.38} = 0.0630$

7) → 3 $x_{1new}^\beta = \frac{(1-K_2 \alpha/\alpha)}{(K_1 \alpha/\alpha - K_2 \alpha)} = 0.207$

$x_{2new}^\beta = 0.793$

$x_{1new}^\alpha = K_1 x_1^\beta = 0.950$ $x_2^\alpha = 0.050$

8) UNIQUAC el..

Target
$x_1^\alpha = 0.927$ $x_1^\beta = 0.369$

(14.17)

water (1) MEK (2) propionic acid (3)

UNIFAC

	A	B	C
$x_3^\alpha =$	0.01,	0.05,	0.10

298.15 K

α

water rich

(1)		(2)		(3)	
H_2O	1	CH_3CO	1	CH_3CO	1
		CH_2	1	OH	1
		CH_3	1		

x 0.999 0.001 1e-11

$\gamma_1^\alpha = 1$ $\gamma_2^\alpha = 44.79$ γ_3^α 7.971

$$x_2^\alpha = \frac{1}{\gamma_2^\alpha} =$$

x 0.001 0.999 1e-11

$\gamma_1^\beta = 23.145$ $\gamma_2^\beta = 1.000$ $\gamma_3^\beta = 1.841$

$K_1 = 23.145$ $K_2 = 0.0223$ $K_3 = 0.231$

$$x_1^B K_1 + (1 - x_1^B) K_2 = 1$$

$$K_1 = \frac{\gamma_1^B}{\gamma_1^\alpha} \quad K = \frac{\gamma_2^B}{\gamma_1^B}$$

$$x_1^B (K_1 - K_2) = 1 - K_2$$

$$x_3^B K_3 + (1 - x_3^B)$$

$$K_3 \frac{\gamma_3^B}{\gamma_3^\alpha}$$

$$x_1^\alpha = x_1^B K_1$$

$$x_1$$

$$x_1^B K_1 + (1 - x_1^B - x_3^B) K_2 = 1$$

$$x_1^B (K_1 - K_2) = 1 - K_2 + x_3^B K_2$$

w/ x_3^B given

(1) $$x_1^B = \frac{1 - K_2 (1 - x_3^B)}{K_1 - K_2}$$

(2) $$x_2^B = 1 - x_1^B - x_3^B$$

(3) $$x_1^\alpha = x_1^B K_1$$

(4) $$x_3^\alpha = x_3^B K_3$$

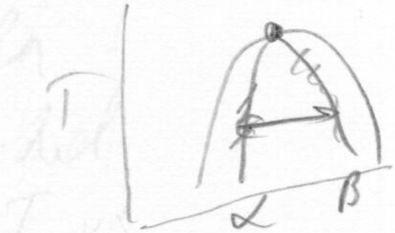
(5) $$x_2^\alpha = 1 - x_1^\alpha - x_3^\alpha$$

HW

14.19

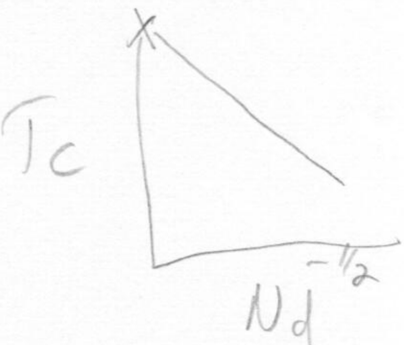
Spinodal formula

- F-H model
- plot T vs. x^{α} x^{β}



$N_d = 1$

$N = 100, 200, 500, 1000$



p. 558

$$\frac{\partial^2 (G/RT)}{\partial n_1^2} = \frac{1}{\phi_1} - \left(1 - \frac{1}{r}\right) - 2(1-\phi) N_{d,1} \chi'$$

$$\chi' = \frac{V_{std} (\delta_1 - \delta_2)^2}{RT}$$

$$V_{std} = V_1 / N_{d,1}$$

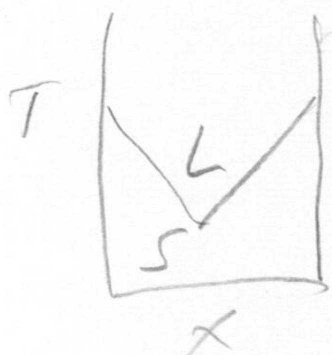
Get x's

calc. y's

get k's

until it doesn't change

HW 14.21



Similar to 14.10

naphthalene(1) biphenyl(2)

Eutectic 39.4°C

$x_{biphenyl} = 0.555$

$x_{naph} = 0.445$

$T_m = 353°K$

$\Delta H_{f\,naphthalene} = 18.8 \frac{kJ}{mole}$

$\Delta H_{f\,biphenyl} = 18.6 \frac{kJ}{mole}$

$T_m = 343°K$

(1) Assume $\gamma_2 = 1$

(2) Solve 14.23 for T

$$x_2 \gamma_2 = \frac{-\Delta H_2^{fus}}{R}\left(\frac{1}{T} - \frac{1}{T_{m2}}\right)$$

⇒ fix x_2 get T

(3) w/ T & x_2 get γ_2 from Unifac

(4) do 2 for T

do until T don't change

then vary x_2

use solver ⇒

2 curves

HW 14.25

50% wt
22.5 mole 0.775
ethylene glycol water

$T_m = 240°K$

(a) ΔH_f water = 333 J/g 18 g/mole = 5999 J/mol
$T_m = 273°K$

$$\ln(x_2 \gamma_2) = -\frac{5994 \text{ J/mol}}{8.13 \text{ J/mol °K}}\left(\frac{1}{T} - \frac{1}{273}\right)$$

x_2 = 0.775

$\gamma_2 = 1$
ideal or debilla → plot γ_2 term unclear, solve for T → get γ_2 from Eq. $\frac{1}{T}$

(b) Negative, T ideal is lower so liquid is favored to solid

(14.28) (21)

phenanthrene @ 20°C

20°C

$$\ln(X_i \gamma_i) = -\frac{\Delta H_{fus}}{R}\left(\frac{1}{T} - \frac{1}{T_{m_i}}\right)$$

$T_m = 372$ °K

$\Delta H_f = 18.6$ KJ/mole

−1.436

$X_i = ?$ find γ_i

using

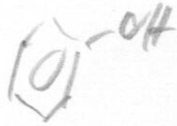
- MAB
- SSCED
- UNIFAC

(14,31) SCE

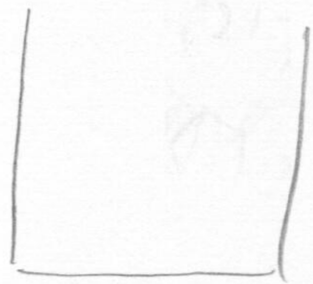
phenol + cyclohexane

(22)

(1)



(2)



(14.35)

α $\beta = 0$

?

MAB?

$\ln \gamma_1 = A_{12} x_2$

$$A_{12} = \frac{(\alpha_2 - \alpha_1)(\beta_2 - \beta_1)(V_1 + V_2)}{4RT}$$

Solid (α_1) · 0 (β_1)

$$\ln(\gamma_1 x_1) = -\frac{\Delta H_f}{R}\left(\frac{1}{T} - \frac{1}{T_{m1}}\right)$$

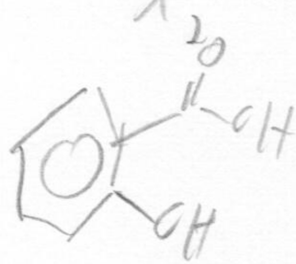
vary x · vary T

in water

$T_m = 432$ °K
$\Delta H_f = 24{,}600$ J/mole

solve γ₁

$$\frac{\ln \gamma_1}{X_2^2} = A_{12}$$



get V from Unifac