Термодинамические модели фаз в системе NaOH-H2O

Индивидуальные соединения

- NaOH (α,β,γ,ж)
- $NaOH \cdot H_2O$
- $NaOH \cdot 2H_2O$
- $NaOH \cdot 3.11H_2O$
- $NaOH \cdot 3.5H_2O$
- $NaOH \cdot 4H_2O$ (α,β)
- $NaOH \cdot 5H_2O$
- $NaOH \cdot 6H_2O$
- $NaOH \cdot 7H_2O$
- H_2O (тв,ж)

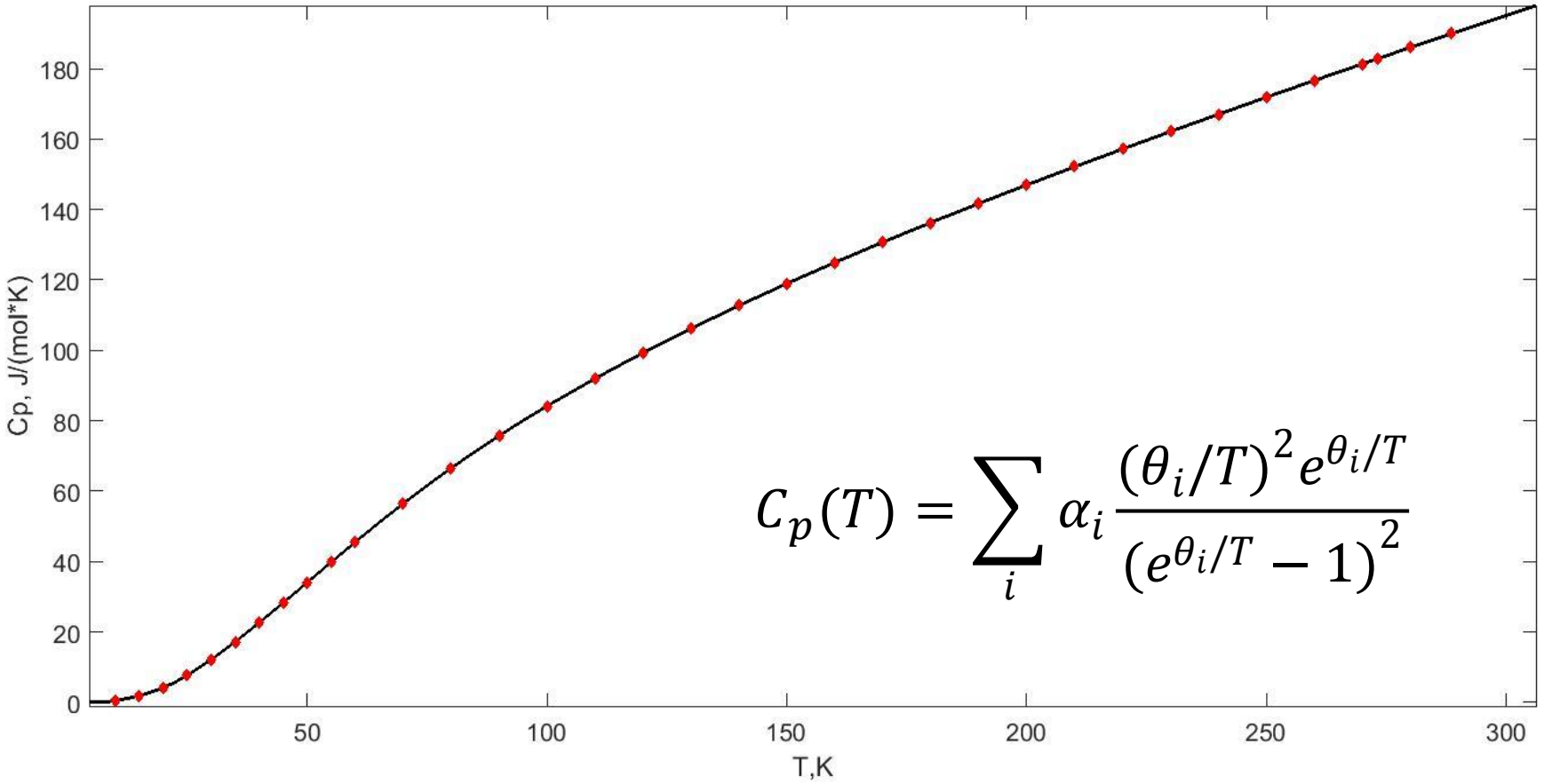
Термодинамическое описание:

$$G = \left(H + \Delta_f H_{298.15}\right) - \mathrm{T} \cdot \left(S + \Delta_f S_{298.15}\right)$$

$$H = \int_{298.15}^{T} Cp dT + \Delta_{tr} H$$

$$S = \int_{298.15}^{T} \frac{Cp}{T} dT + \Delta_{tr} H / T_{tr}$$

Описание Cp(T), пример: $NaOH \cdot 3.5H_2O$



$$C_p(T) = \sum_i \alpha_i \frac{(\theta_i/T)^2 e^{\theta_i/T}}{(e^{\theta_i/T} - 1)^2}$$

Энтальпии образования гидратов

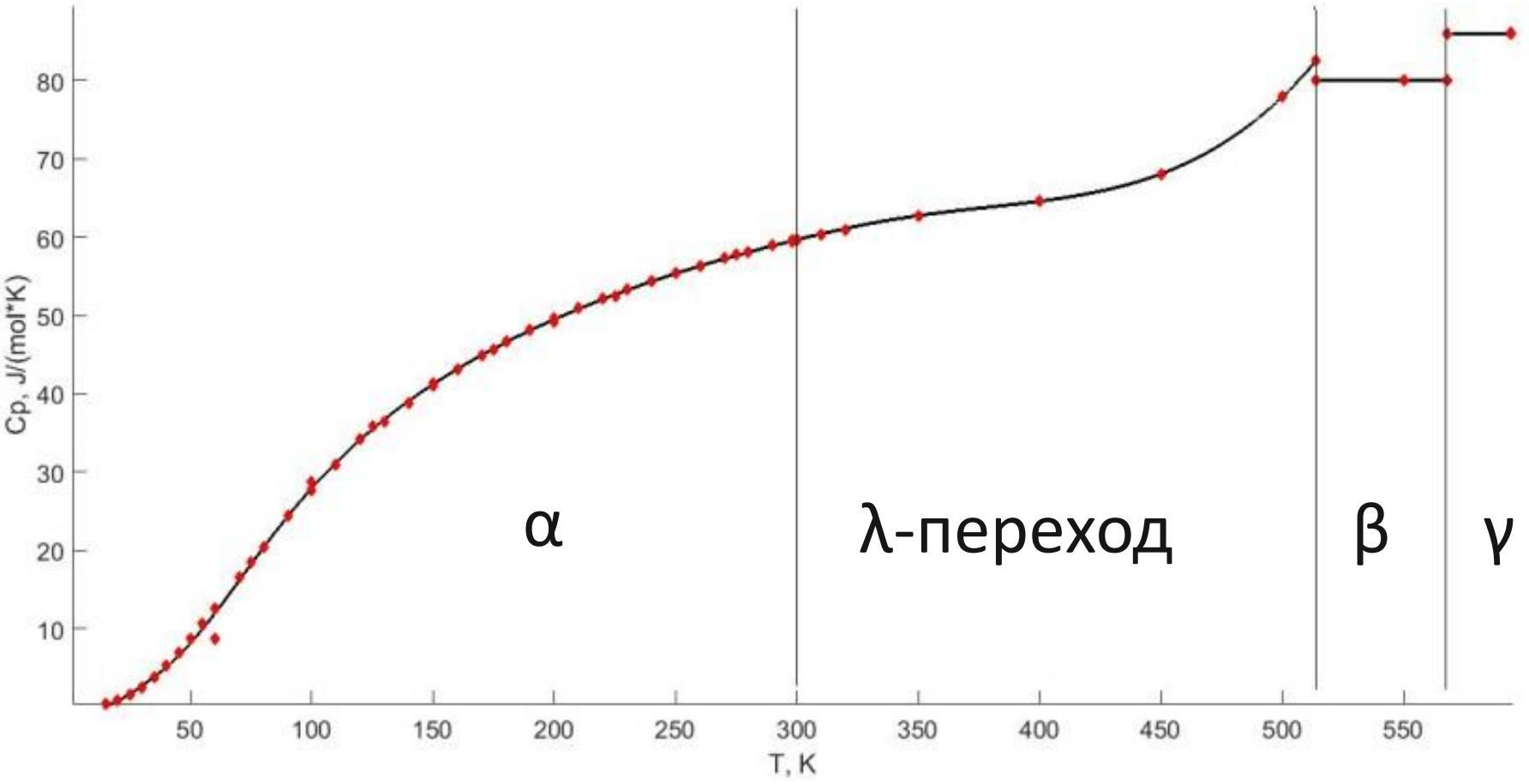
$$NaOH(s) + AH_2O(l) = NaOH \cdot AH_2O(ph)$$

A	ph	$-\Delta_r H$	$-\Delta_r S$
0	s	0	0
1	s	23091	34.84
2	l	21774	8.24
3	l	30526	19.00
3.5	l	33719	22.80
4	l	36196	25.43
5	l	39510	27.95
7	l	42572	27.52

S_{res}?

J, mol, K, при 298.15 K

Описание Cp(T), NaOH



Раствор $NaOH$-H_2O

- Модель Клегга

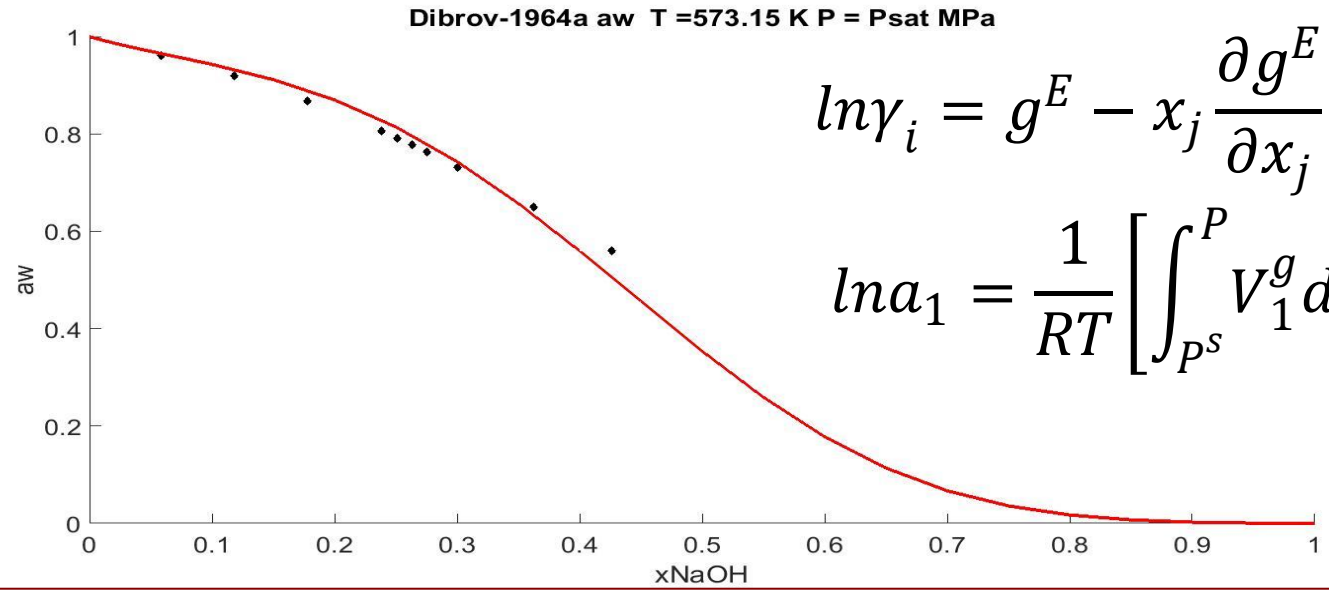
$$g^E = f(PAR, x_2) = -\frac{4I_x}{\rho}\ln\left(1+\rho I_x^{0.5}\right)A_x + \frac{x_2^2}{4}g\left(\alpha I_x^{0.5}\right)B_{MX} - x_2^2 W_{1,MX} + x_1 x_2^2 U_{1,MX} + x_1^2 x_2^2 V_{1,MX}$$

$$x_1 = \frac{n_1}{n_1 + 2n_2} \quad x_2 = \frac{2n_2}{n_1 + 2n_2} \quad I_x = x_2/2$$

$$g(y) = 2[1 - (1+y)exp(-y)]/y^2$$

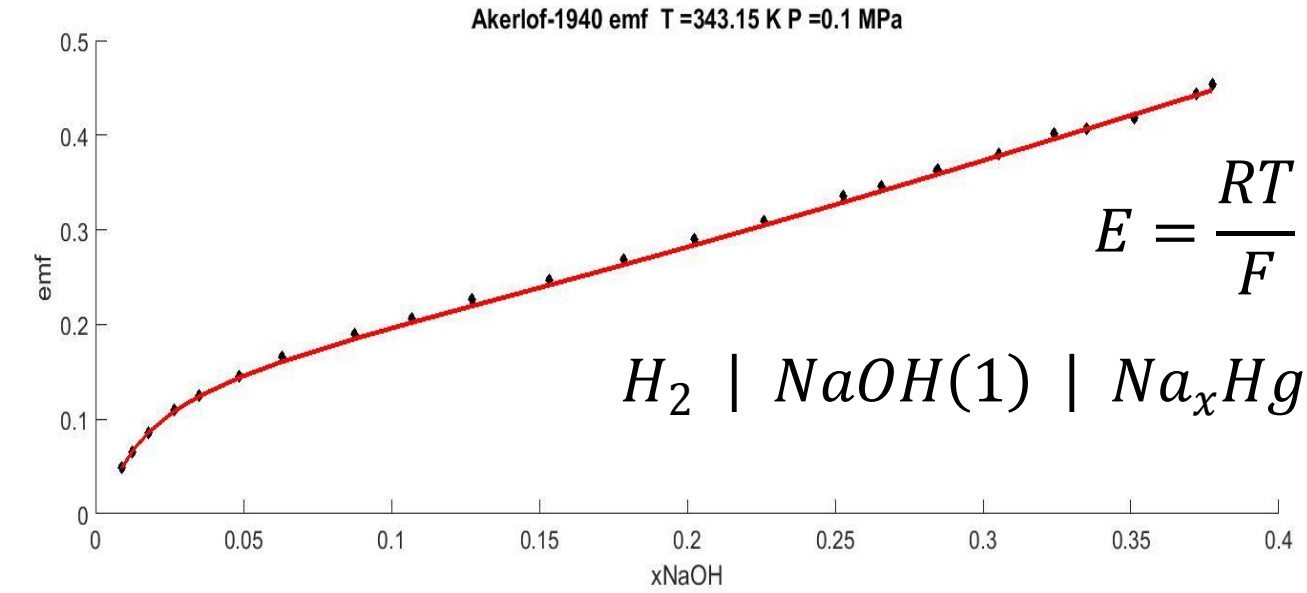
- Ассиметричная нормировка
- Расчет на 1 моль частиц ($n_1+2n_2=1$)

Активности и ЭДС



$$ln\gamma_i = g^E - x_j \frac{\partial g^E}{\partial x_j}$$

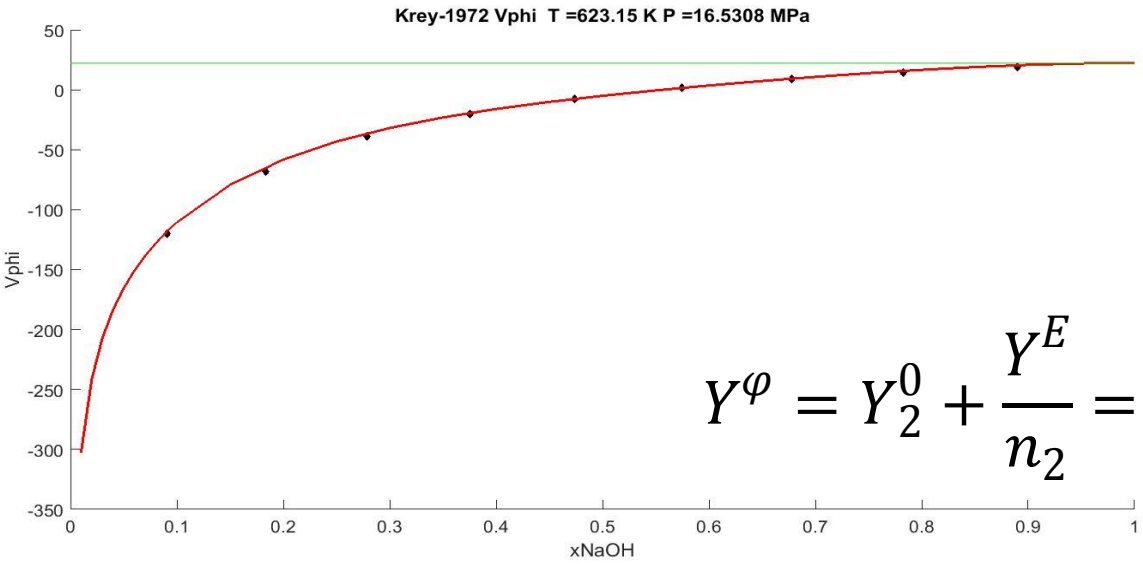
$$lna_1 = \frac{1}{RT}\left[\int_{P^s}^{P} V_1^g dP - V_1^l (P - P^s)\right]$$



$$E = \frac{RT}{F} ln\left(\frac{a_2(1)a_1(2)}{a_1(1)a_2(2)}\right)$$

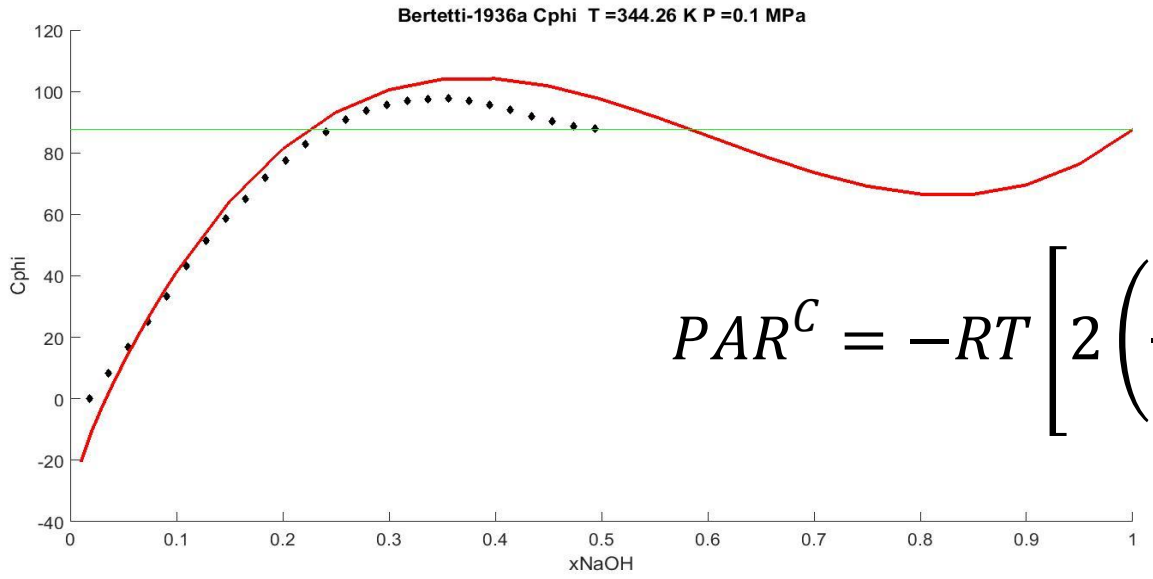
$$H_2 \mid NaOH(1) \mid Na_xHg \mid NaOH(2) \mid H_2$$

Кажущиеся величины



$$Y^{\varphi} = \frac{(Y - n_1 Y_1^0)}{n_2}$$

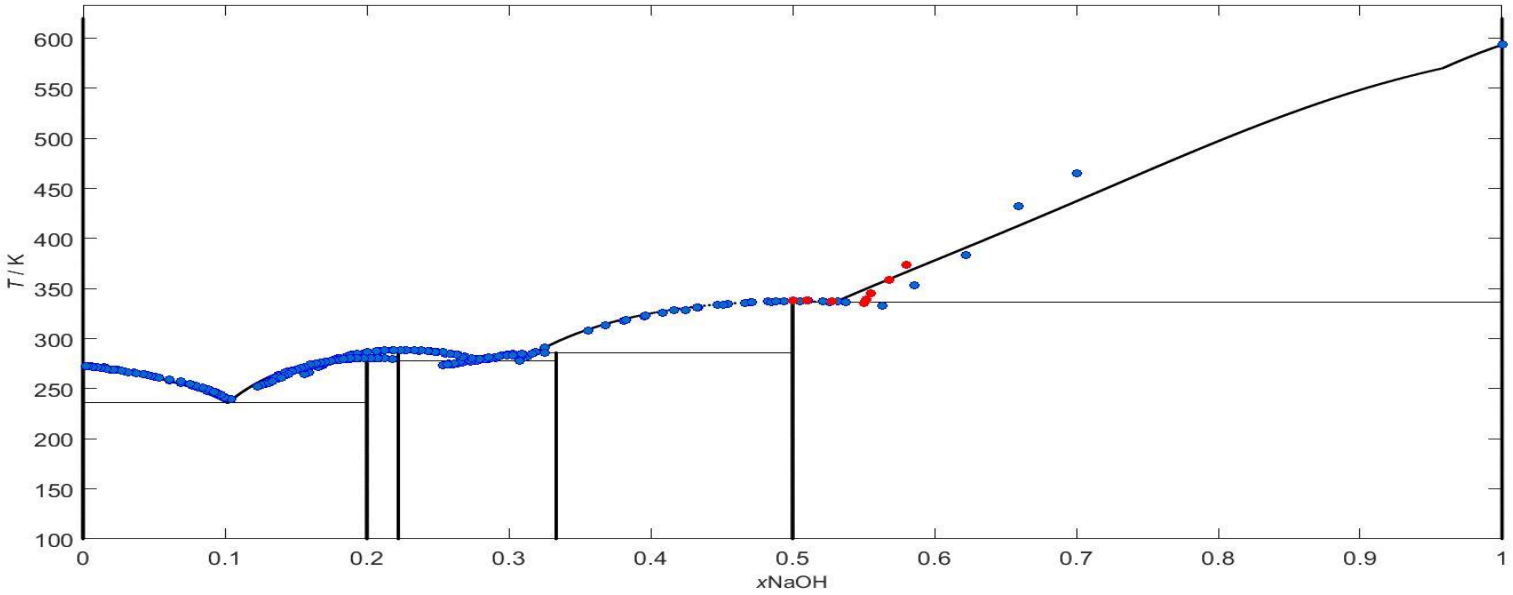
$$Y^{\varphi} = Y_2^0 + \frac{Y^E}{n_2} = Y_2^{liq} + 2\frac{Y^E}{x_2} - 2Y^E(x_2 = 1)$$

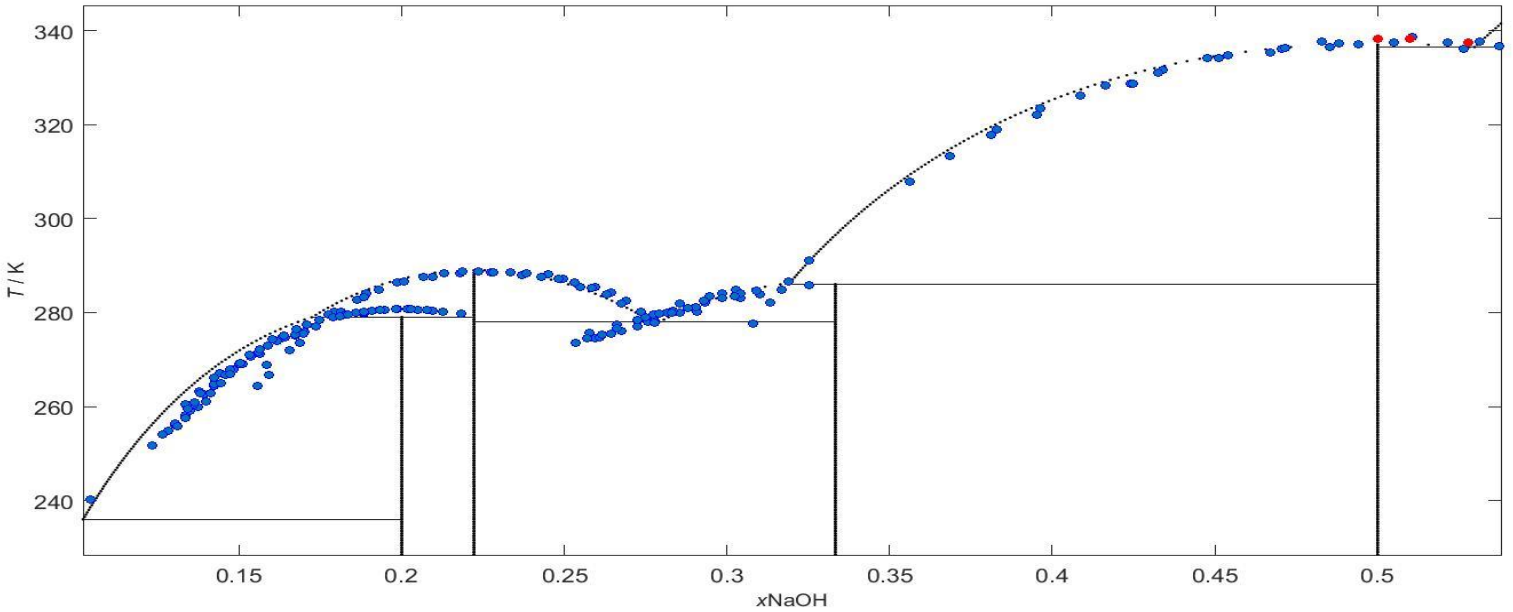


$$Y^E = f(PAR^Y, x_2)$$

$$PAR^C = -RT\left[2\left(\frac{\partial PAR}{\partial T}\right)_P + T\left(\frac{\partial^2 PAR}{\partial T^2}\right)_P\right]$$

Равновесие жидкость-твердое





Спасибо за внимание!