TERMODINÂMICA DAS SOLUÇÕES

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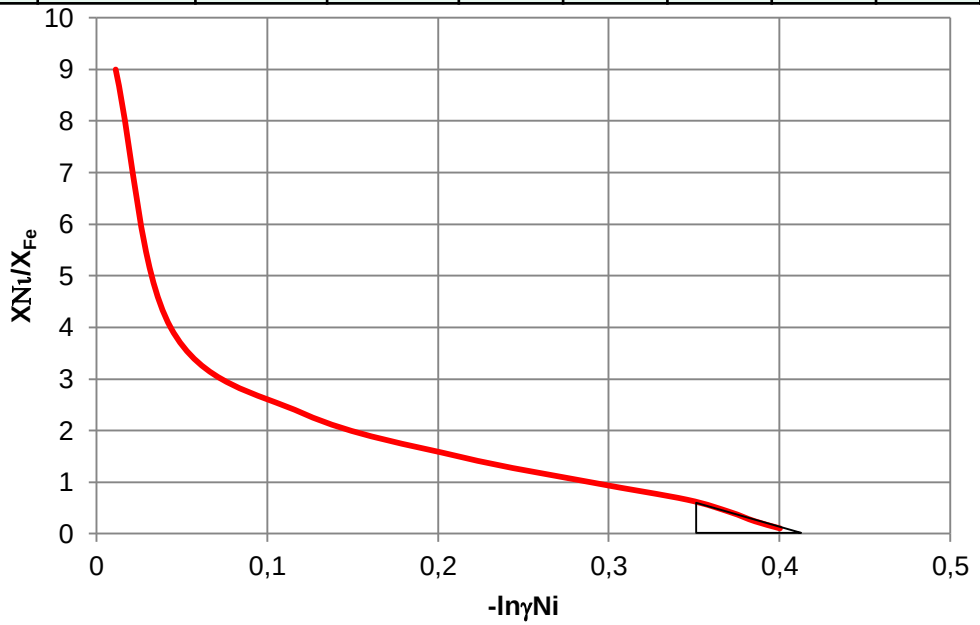
As atividades do Ni nas ligas Fe-Ni líquidas a 1600°C foram determinadas e estão apresentadas na tabela a seguir. Determine a atividade do Fe para X_{Fe}=0,6.

X_{Ni}	1,00	0,90	0,80	0,70	0,60	0,50	0,40	0,30	0,20	0,10
a_{Ni}	1,00	0,89	0,766	0,62	0,485	0,374	0,283	0,207	0,136	0,067

X_{Ni}	1	0,9	0,8	0,7	0,6	0,5	0,4	0,3	0,2	0,1	0
a_{Ni}	1	0,89	0,77	0,62	0,49	0,37	0,28	0,21	0,14	0,07	0
γ_{Ni}	1	0,99	0,96	0,89	0,81	0,75	0,71	0,69	0,68	0,67	0,66
$-\ln\gamma_{Ni}$	0	0,01	0,04	0,12	0,21	0,29	0,35	0,37	0,39	0,4	
X_{Ni}/X_{Fe}		9	4	2,33	1,5	1	0,67	0,43	0,25	0,11	0



A=(0,41-0,35)*0,67*0,5=0,158

Portanto, $-\ln\gamma_{Fe}$=0,158 e γ_{Fe}=0,98

Consequentemente: a_{Fe}=0,98*0,6=0,59

Determinar a atividade raoultiana do silício numa liga líquida Fe-Si a 1600°C contendo 1%Si. Admitir válida a lei de Henry para o Si. Fazer o mesmo cálculo considerando que a LH não é válida

- tabelas termodinâmicas: $\gamma_{Si}^{o} = 0{,}0013$; $\varepsilon_{Si}^{Si} = 12{,}6$; $\rho_{Si}^{Si} = -5{,}741$

- massas atômicas (g/mol): Fe = 55,85; Si = 28,09

$$a_i = \gamma_{Si}^{o}.X_{Si} = 0{,}0013x0{,}019688 = 0{,}0000256$$

$$\ln \gamma_{Si} = \ln \gamma_{Si}^{\circ} + \varepsilon_{Si}^{Si}.X_{Si} + \rho_{Si}^{Si}.X_{Si}^{2}$$

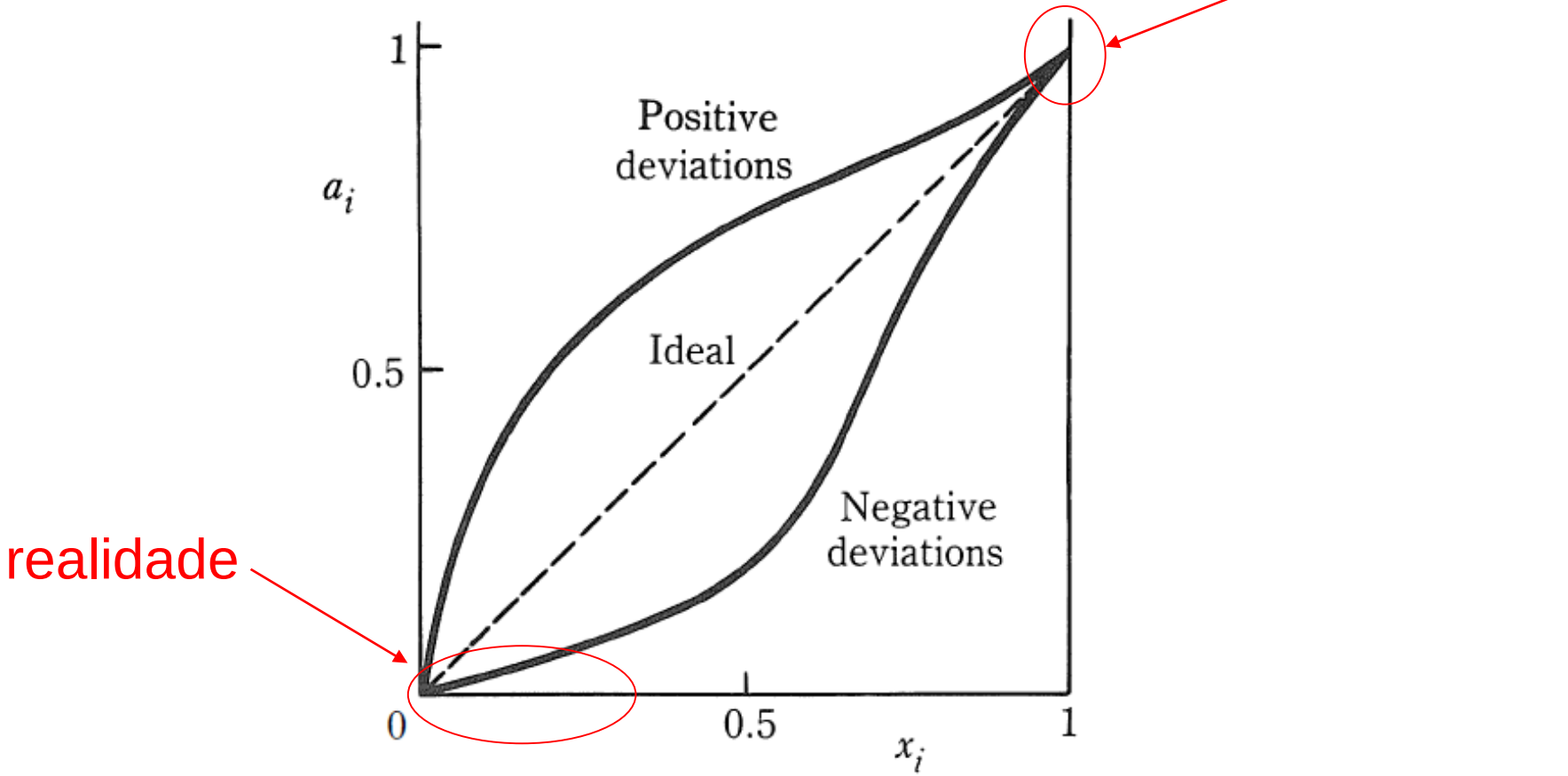
$$a_{Si} = \gamma_{Si}.X_{Si} = 0{,}001666x0{,}019688 = 0{,}0000328$$

$$a_{Si} = \gamma_{Si}.X_{Si} = 0{,}001662x0{,}019688 = 0{,}0000327$$

ABORDAGEM TECNOLÓGICA

ESCALAS DE ATIVIDADE -HENRIANA-

- A referência raoultiana está muito distante das situações usuais (soluções diluídas)



ESCALAS DE ATIVIDADE -HENRIANA-

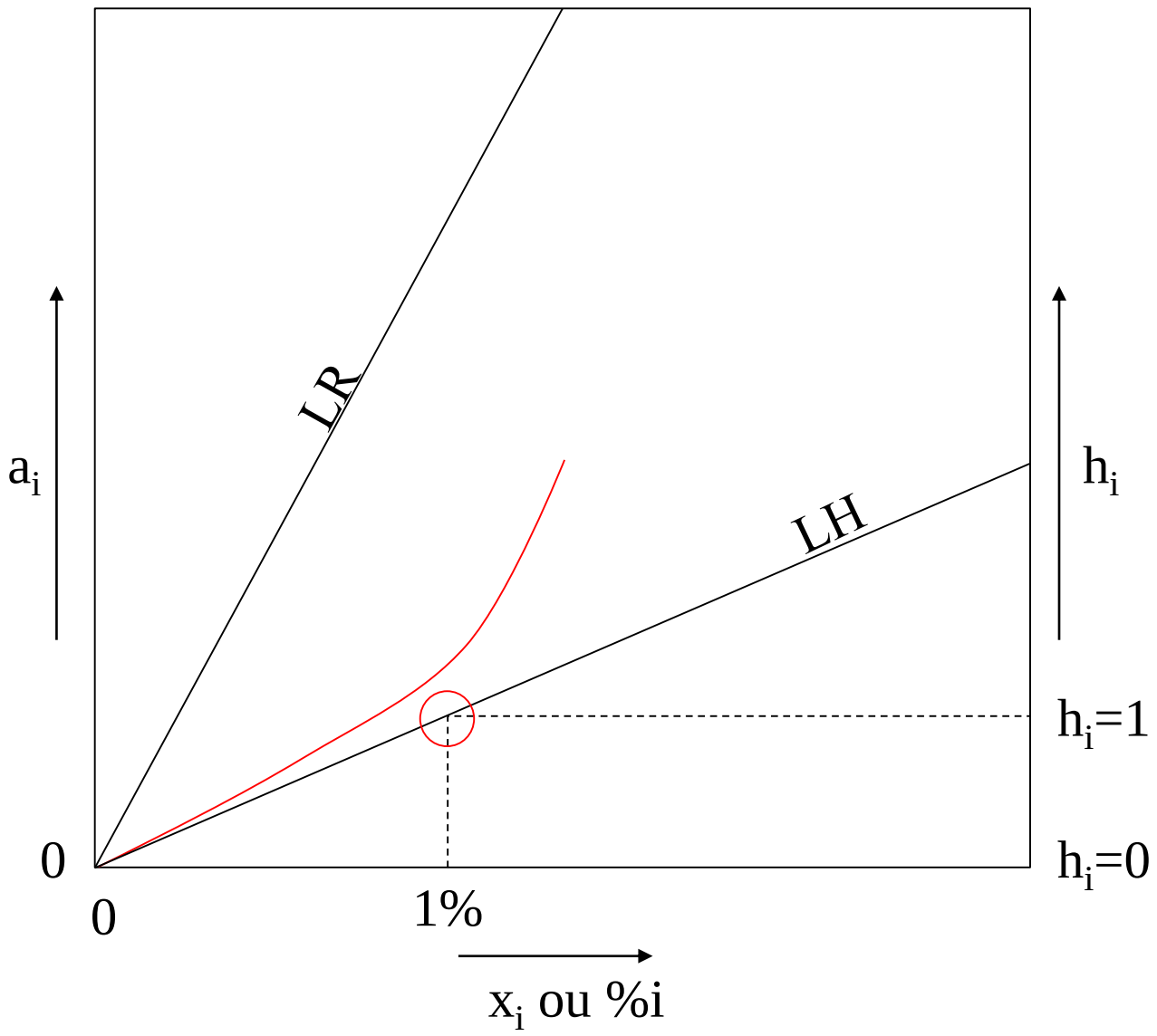
- A concentração em X_i não é comum do ponto de vista tecnológico

C %	Mn %	Cr %	Mo %	W %	V %	OUTROS %
0,90	0,30	4,20	5,00	6,20	1,90	-

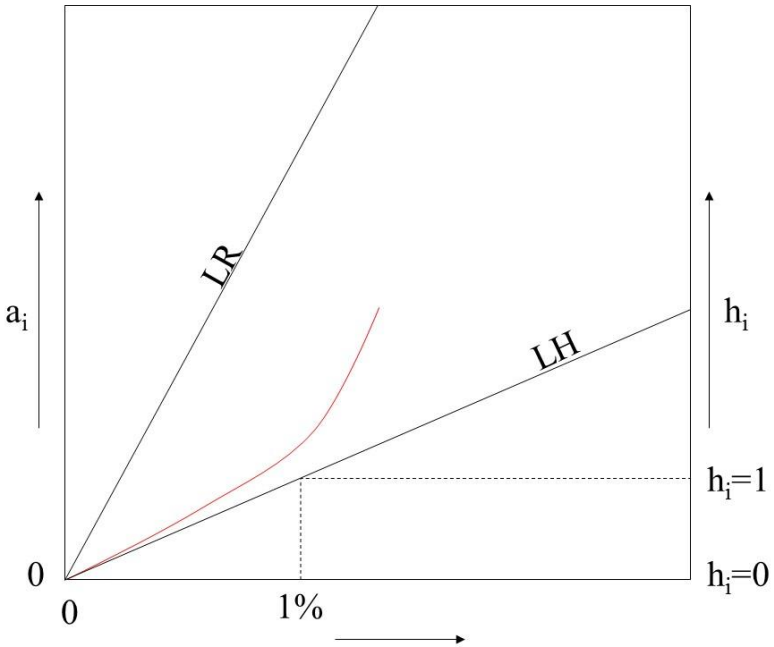
- Nova Escala: baseada ou referenciada na Lei de Henry
  - É válida, a princípio, para as soluções infinitamente diluídas
  - Consideram-se duas concentrações de referência
    - 1% (mais utilizada em metalurgia e materiais): **h**
    - 1 molar: **a'**
- Dever ser sempre lembrado que as tabelas de energia livre sempre consideram o estado raoultiano (i puro ou p_i=1atm)

< > sólido; { } líquido ; ( ) gás	$\Delta G^o = \Delta H^o - T.\Delta S^o$		faixa de T	
reação	ΔH^o (cal/mol)	ΔS^o (cal/mol.K)	(^oC)	
<Al> = {Al}	2.580	2,76		660
{Al} = (Al)	72.810	26,17	660	2520
<AlN> = {Al} + 1/2 (N_2)	78.170	27,61	660	2000
<Al_2O_3> = 2 {Al} + 3/2 (O_2)	403.260	78,11	660	2054
<C> = (C)	170.520	37,16	1750	3800
(CH_4) = <C> + 2 (H_2)	21.760	26,45	500	2000
(CO) = <C> + 1/2 (O_2)	27.340	-20,50	500	2000
(CO_2) = <C> + (O_2)	94.490	-0,13	500	2000
<Ca> = {Ca}	2.040	1,84		839
{Ca} = (Ca)	37.720	20,82	839	1491
<CaF_2> = {CaF_2}	7.100	4,20		1418
{CaF_2} = (CaF_2)	73.780	26,29		2533
<CaF_2> = {Ca} + (F_2)	291.400	38,79	839	1484
<CaC_2> = {Ca} + 2 <C>	14.400	-6,28	839	1484
<$CaCO_3$> = <CaO> + (CO_2)	38.560	32,80	700	1200
<CaSi> = <Ca> + <Si>	36.000	3,70	25	839

ESCALA HENRIANA- 1%



ESCALA HENRIANA- 1%



$$h_i = \frac{X_i . P_{Total}}{X_i^{1\%} . P_{Total}} = \frac{X_i}{X_i^{1\%}}$$

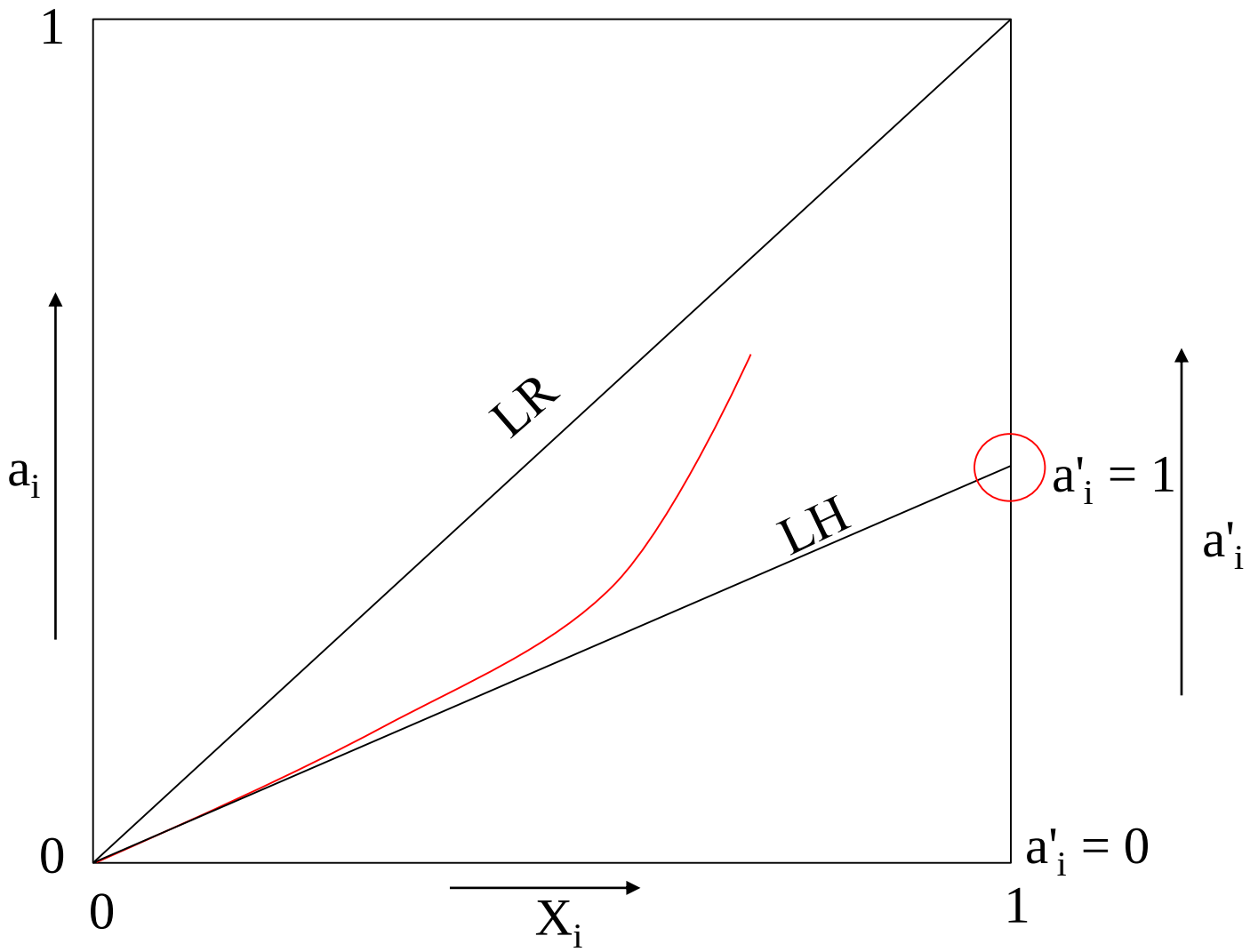
$$h_i = \frac{\%i}{\%i^{1\%}}$$

$$\boldsymbol{h_i = \%i}$$

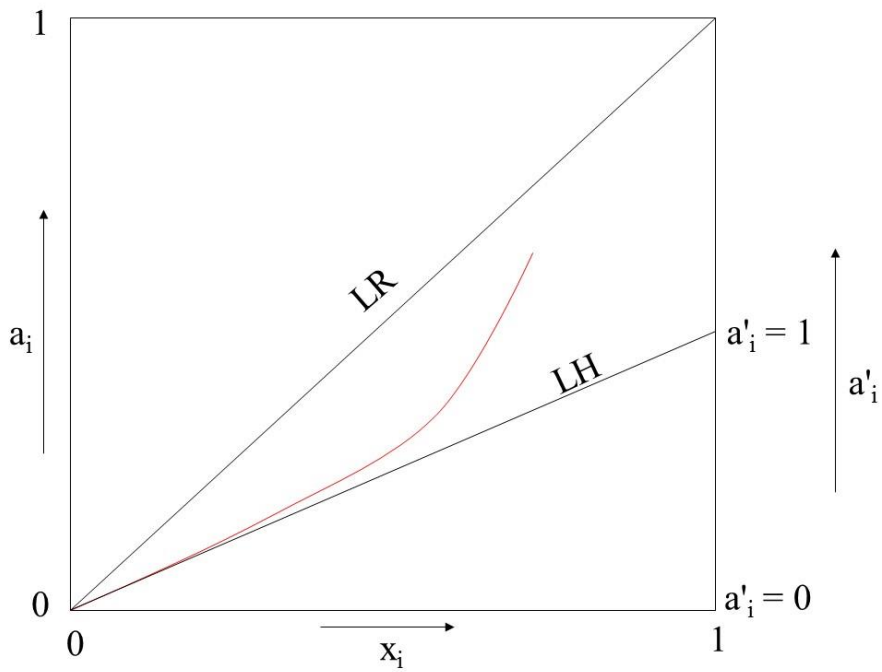
Válida a LH

$$a_i^{1\%} = \frac{p_i}{p_i^{1\%}} = h_i$$

ESCALA HENRIANA- 1molar



ESCALA HENRIANA- 1molar



$$a'_i = \frac{x_i . P_{Total}}{x_i^{x=1} . P_{Total}} = \frac{X_i}{X_i^{X=1}} = X_i$$

$$a_i^{x=1} = \frac{p_i}{p_i^{X=1}} = a'_i$$

$$\boldsymbol{a'_i = X_i}$$

Válida a LH

$$X_i = \frac{n_i}{n_j + n_i} = \frac{\frac{m_i}{M_i}}{\frac{m_j}{M_j} + \frac{m_i}{M_i}} = \frac{\frac{\%i}{M_i}}{\frac{\%j}{M_j} + \frac{\%i}{M_i}}$$

$$Para\ \%i \rightarrow 0\% \Rightarrow\ \%j \rightarrow 100\%$$

$$X_i = \frac{\frac{\%i}{M_i}}{\frac{100}{M_j} + \frac{0}{M_i}} = \frac{\frac{\%i}{M_i}}{\frac{100}{M_j}}$$

$$X_i = \frac{\%i.M_{solvente}}{100.M_i}$$

i pu

$K =$

Se válida a lei de Henry n
considerado:

- $\boldsymbol{X_i = \frac{\%i.M_{solvente}}{100.M_i}}$
- **%i = 1**
- $\boldsymbol{\gamma_i = \gamma_i^o}$

$$K = \frac{100.M_i}{\gamma_i^o.M_{solvente}}$$

j = solvente

$i_{puro} = i_{1\%}$

$$\Delta G^{o}_{R\rightarrow h(1\%)} = R.T\ln(\frac{\gamma_i^o.M_j}{100.M_i})$$

Se $\ln\gamma^o = A+B/T$

$$\Delta G^{o}_{R\rightarrow h(1\%)} = B.R + R.T.\left[A + \ln(\frac{M_j}{100.M_i})\right]$$

$$\Delta H^{o}_{R\rightarrow h(1\%)} = B.R$$

$$\Delta S^{o}_{R\rightarrow h(1\%)} = -R\left[A + \ln(\frac{M_j}{100.M_i})\right]$$

$i_{puro} = i_{X=1}$

$$\Delta G^{o}_{R\rightarrow h(X=1)} = R.T\ln(\gamma_i^{o})$$

Se $\ln\gamma^{o} = A+B/T$

$$\Delta G^{o}_{R\rightarrow h(X=1)} = B.R + R.T.A$$

$$\Delta H^{o}_{R\rightarrow h(X=1)} = B.R$$

$$\Delta S^{o}_{R\rightarrow h(X=1)} = -A.R$$

ESCALA HENRIANA

$i_{raoultiano} = i_{henriano}$

Element, i†	γ_i^0(1873)*	M (pure) = M(*i.d.*, X, liq.) $\Delta G(x)$, cal/g atom	M (pure) = M(*i.d.*, wt.-%, liq.) $\Delta G(\%)$, cal/g atom	Ref. and Notes
Ag (*l*)	200	19 700	19 700 − 10·46T	11, 2; from solubility data, regular solution is assumed.
Al (*l*)	0·029	−15 100 + 1·03T	−15 100 − 6·67T	19
B (*s*)	0·022	−15 600 + 0·71T	−15 600 − 5·15T	29: from solubility of BN, using values for nitrogen given below.
C (*gr*)	0·57	5 400 − 4·0T	5 400 − 10·1T	42, 2
Ca (*v*)	2240	− 9 430 + 20·3T	− 9 430 + 11·8T	20; from solubility data, regular solution is assumed.
Co (*l*)	1·07	240	240 − 9·26T	82, 2; regular solution is assumed.
Cr (*l*)	1·0	0	− 9·01T	87, 86, 88, 89; liquid Fe–Cr alloys ideal at low Cr concentration.
Cr (*s*)	1·14	4 600 − 2·19T	4 600 − 11·20T	
Cu (*l*)	8·6	8 000	8 000 − 9·41T	93, 2
1/2 H_2 (g)	—	—	8 720 + 7·28T	95, 96, 2; ΔG°(ppm) = 8,720–11·02T
Mn (*l*)	1·3	976	976 − 9·12T	125, 126, 2
Mo (*l*)	1	0	− 10·23T	Ideal behaviour assumed.
Mo (*s*)	1·86	6 600 − 2·29T	6 600 − 12·52T	Ideal behaviour of liquid solution, transfer of standard state.
1/2 N_2 (g)	—	—	860 + 5·71T	135
Nb (*l*)	1·0	0	− 10·2	See Mo above.
Nb (*s*)	1·4	5 500 − 2·3T	5 500 − 12·5	
Ni (*l*)	0·66	− 5 000 + 1·80T	− 5 000 − 7·42T	164, 2
1/2 O_2 (g)	—	—	−28 000 − 0·69T	168
1/2 P_2 (g)	—	—	−29 200 − 4·6T	218
Pb (*l*)	1400	50 800 − 12·7T	50 800 − 25·4T	21; calculated from data on solubility.
1/2 S_2 (g)	—	—	−32 280 + 5·6T	72
Si (*l*)	0·0013	−31 430 + 3·64T	−31 430 − 4·12T	16, 243
Sn (*l*)	2·8	3 820	3 820 − 10·62T	244; regular solution assumed.
Ti (*l*)	0·037	−11,100	−11 000 − 8.85T	19; regular solution assumed.
Ti (*s*)	0·038	− 7 440 − 1·90T	− 7 440 − 10·75T	19
U (*l*)	0·027	−13 400	−13 400 − 12·0T	24; regular solution assumed.
V (*l*)	0·08	−10 100 + 0·37T	−10 100 − 8·6T	28
V (*s*)	0·1	− 4 950 − 1·93T	− 4 950 − 10·9T	
W (*l*)	1	0	− 11·5T	Assumed ideal liquid solution.
W (*s*)	1·2	+ 7 500 − 3·65T	+ 7 500 − 15·2T	
Zr (*l*)	0·037	−12 200	−12 200 − 10·13T	γ^0_{Zr} assumed equal to γ^0_{Ti}, and regular solution assumed.
Zr (*s*)	0·043	− 8 300 − 1·82T	− 8 300 − 11·95T	

* $\gamma_i^0 = \lim_{X_i \to 0} a_i/X_i$

† The letters in parentheses indicate the standard states used. All are of one atmosphere pressure.

1 cal = 4·18 J

Determinar a atividade raoultiana do silício numa liga líquida Fe-Si a 1600ºC contendo 1%Si. Admitir válida a lei de Henry para o Si.

$$\{Si\} = \underline{Si} \qquad \Delta G° = -31430 - 4{,}12T(cal/mol)$$

$$\Delta G^{o}_{1873K} = -3{,}91x10^{4} cal/mol \qquad K_{1873K} = \frac{h_{Si}}{a_{Si}} = \frac{1}{a_{Si}} = 3{,}7x10^{4}$$

$$\boxed{a_{Si} = 2{,}7x10^{-5}}$$

$$a_i = \gamma^{o}_{Si}.X_{Si} = 0{,}0013x0{,}019688 = 0{,}0000256$$