INTERNATIONAL ATOMIC ENERGY AGENCY
UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION
INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
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SMR/382- 24

WORKSHOP ON SPACE PHYSICS:
"Materials in Micorgravity"
27 February - 17 March 1989

"Capillarity and Materials Properties" - II

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SURFACE TENSION AND ADSORPTION IN METAL-OXYGEN SYSTEMS.

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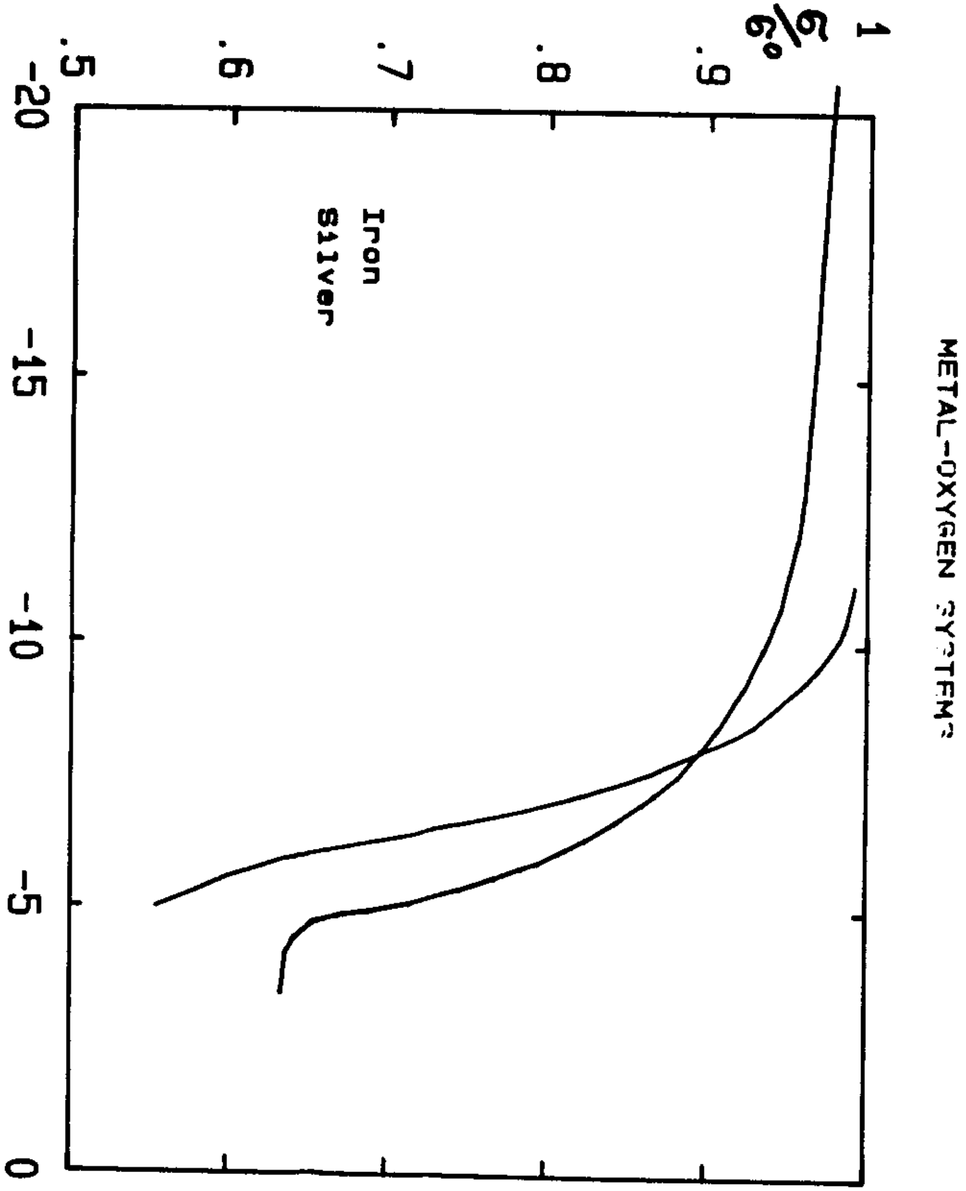
The surface tension of liquid metals is very sensitive to Oxygen adsorption.

Experimental investigations on Ag, Fe, Ni, Co and Sn have shown that the surface tension of these metals is strongly reduced (even up to 50%) by small oxygen bulk concentrations (X << 0.01%).

However, the eperimental results are very scanty and refer , practically, only to the systems mentioned above .

It is therefore necessary to look for a theoretical explication of the relationships existing between oxygen surface activity and its solubility.



FOUNDAMENTAL RELATIONSHIPS

-SYSTEM :

- Liquid-Vapour
- Two components
- Equilibrium
- Constant volume
- Constant temperature

ADSORPTION OF COMP. 2 AT LIQUID-VAPOUR SURFACE

$$\Gamma_2 = \frac{n_2^\sigma}{A} \qquad n_2^\sigma = n_{TOT} - n_2$$

-RELATIVE ADSORPTION (indepen. of dividing surf.)

$$\Gamma_{2,1} = \Gamma_2 - \Gamma_1 \frac{x_2}{x_1}$$

-SURFACE TENSION ( ) AND SURFACE COMPOSITION ($\Gamma_{2,1}$)
are correlated by GIBBS ADSORPTION ISOTHERM:

$d\sigma = -s^\sigma dT - \sum_i \Gamma_i d\mu_i$, or, in terms of $\Gamma_{2,1}$, at T=const.:

$$\Gamma_{2,1} = -\left(\frac{\partial\sigma}{\partial\mu_2}\right)_T = -\frac{1}{RT}\left(\frac{\partial\sigma}{\partial \ln a_2}\right)_T$$

-$\Gamma_{2,1}$ may be obtained from the dependence of the surface tension on the activity of the solute 2 at any given temperature.

This equation is the basis for most adsorption measurements associated with liquid solutions.

MODELS

-THERMODINAMIC MACROSCOPIC MODELS

-PERFECT SOLUTION MODEL OF AN INTERFACE
(=bulk ideal)

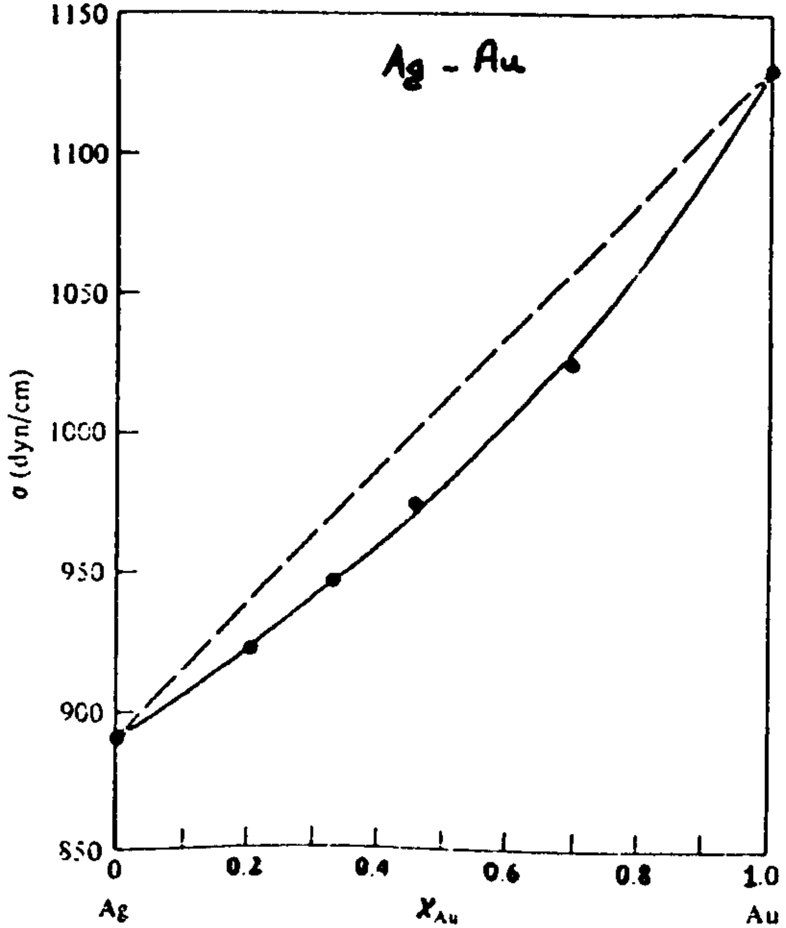
HYPOTHESIS :

- Interface as a monolayer
- No interactions between atoms
- Atoms of similar size
- Random distribution

This model gives:

$$\sigma = \sigma_i + \frac{RT}{\Omega} \ln \frac{X_i^m}{X_i}$$

The model is valid for some metallic solutions as Ag-Au , Cu-Ni , Au-Bi, Ge-Bi ....
Generally this model is not satisfactory.



LANGMUIR ISOTHERM MODEL

HYPOTHESIS   like model above and

Number of surf.sites limited

Final equation is:

$$\sigma = \sigma_1 + RT\,\Gamma_{2,1}^{SAT} \ln(1 - \vartheta)$$

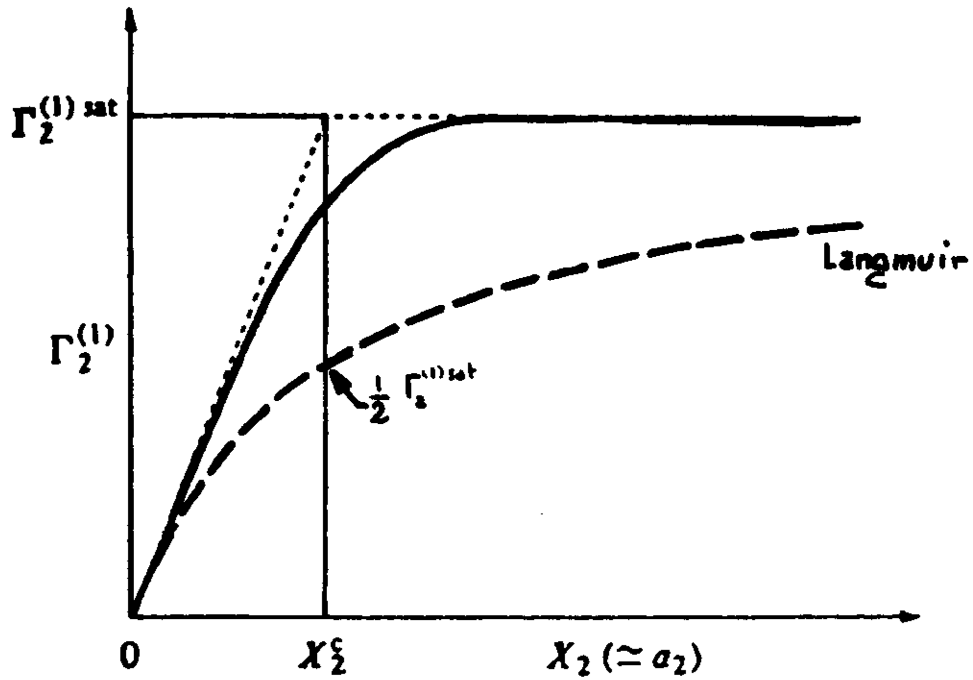
The model is not valid for reactive gases.

In fact for X2 = X2c -----> $\Gamma_{2,1} = \frac{1}{2}\Gamma_{2,1}^{SAT}$

In the cases examined

for X2 = X2c -----> $\Gamma_{2,1} \gg \frac{1}{2}\Gamma_{2,1}^{SAT}$

(see FIG.)



-IMPROVEMENT OF FOWLER-GUGGENHEIM MODEL

HYPOTESIS

- Monolayer
- Nearest neighbours interactions
- Metal-Oxygen inter. parameters from dissolution enthalpy
- Metallic atoms interactions from evaporation enthalpy
- Relative adsorption $\Gamma_2 = \Gamma_{2,1}$
- Surface 'exclusion rule'

considering the adsorption reaction:

$$\text{Obulk} + \text{Vsup} = \text{Osup}$$

the 'equilibrium constant' is :

$$K = \frac{\Gamma_2}{a_2 (M - f \Gamma_2)} \exp \frac{-\Delta E}{RT}$$

where

M = number of moles of Oxygen on a surface monolayer.

ΔE = Eb − Es

f = surface structure coeff.

if a surface compound $Me_x O_y$ can form, then

$$f = (x + y) / y$$

The energetic term can be written as :

$$\Delta E = 1/2\ Z\ m\ \varepsilon_{21} + 1/2\ Z\ l\ f\ \Theta\ (\varepsilon_{21} - \varepsilon_{12})$$

and putting

$$1/2\ Z\ \varepsilon_{11} = -\text{Hivap} \quad , \quad 1/2\ Z\ \varepsilon_{21} - 1/2\ Z\ \varepsilon_{11} = \text{Hdiss}$$

we obtain:

$$\Delta E = \alpha f \Theta + \beta$$

with

β = (Hdiss − Hivap) * m

α = (Hdiss − Hivap − 1/2 Z ε_{22}) * l

m = nearest neighbours fraction across two planes

l = nearest neighbours fraction in the plane

Z = coordination number

Putting in the 'equilibrium constant' the value obtained from Gibbs adsorption equation , we get

$$* \qquad d\sigma = -RTM \frac{K\,da}{Kfa + \exp\left(-\frac{\Delta E}{RT}\right)}$$

This equation may be integrated taking into account:

a) A linear variation of the energetic term with $\theta = \Gamma_2/M$

b) f = constant

The integration leads to the final formula :

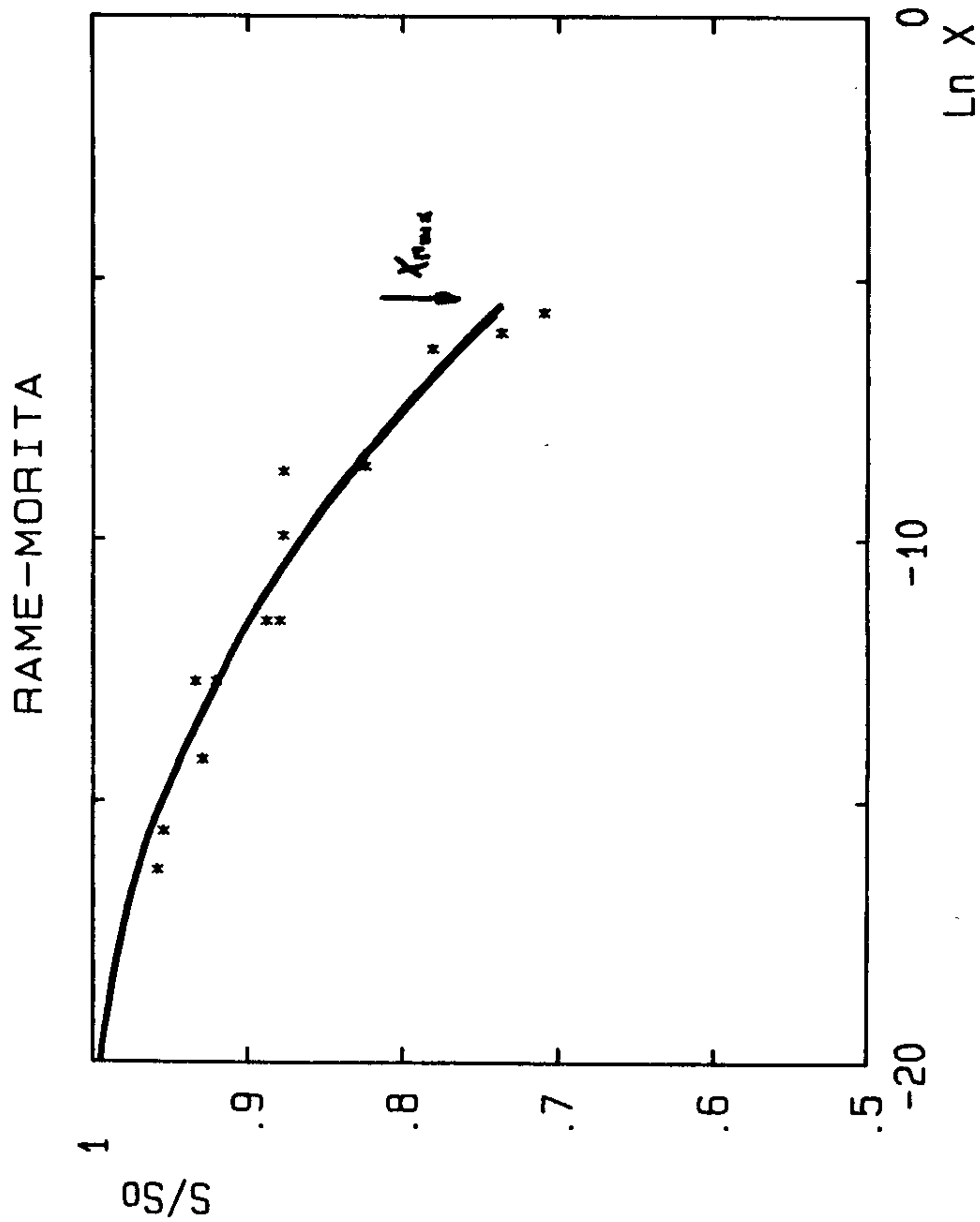
$$** \qquad \sigma = \sigma^{\circ} + RTM \left\{ \frac{\alpha f \theta^2}{2\,RT} + \frac{1}{f} \ln\left(1 - f\theta\right) \right\}$$

where σ° = surface tension of the pure metal

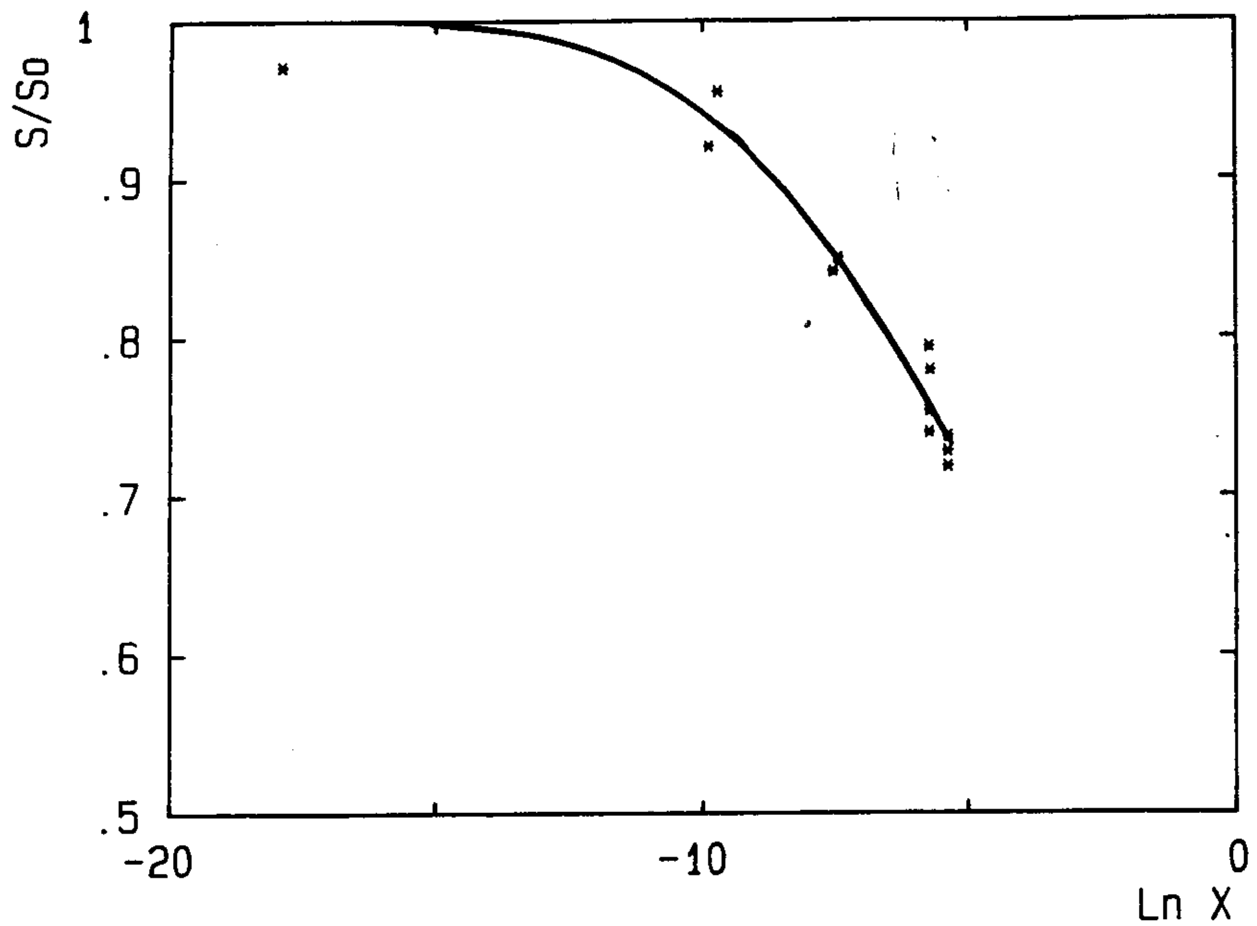
Equation ** :

1) shows the variation of surface tension with adsorption.

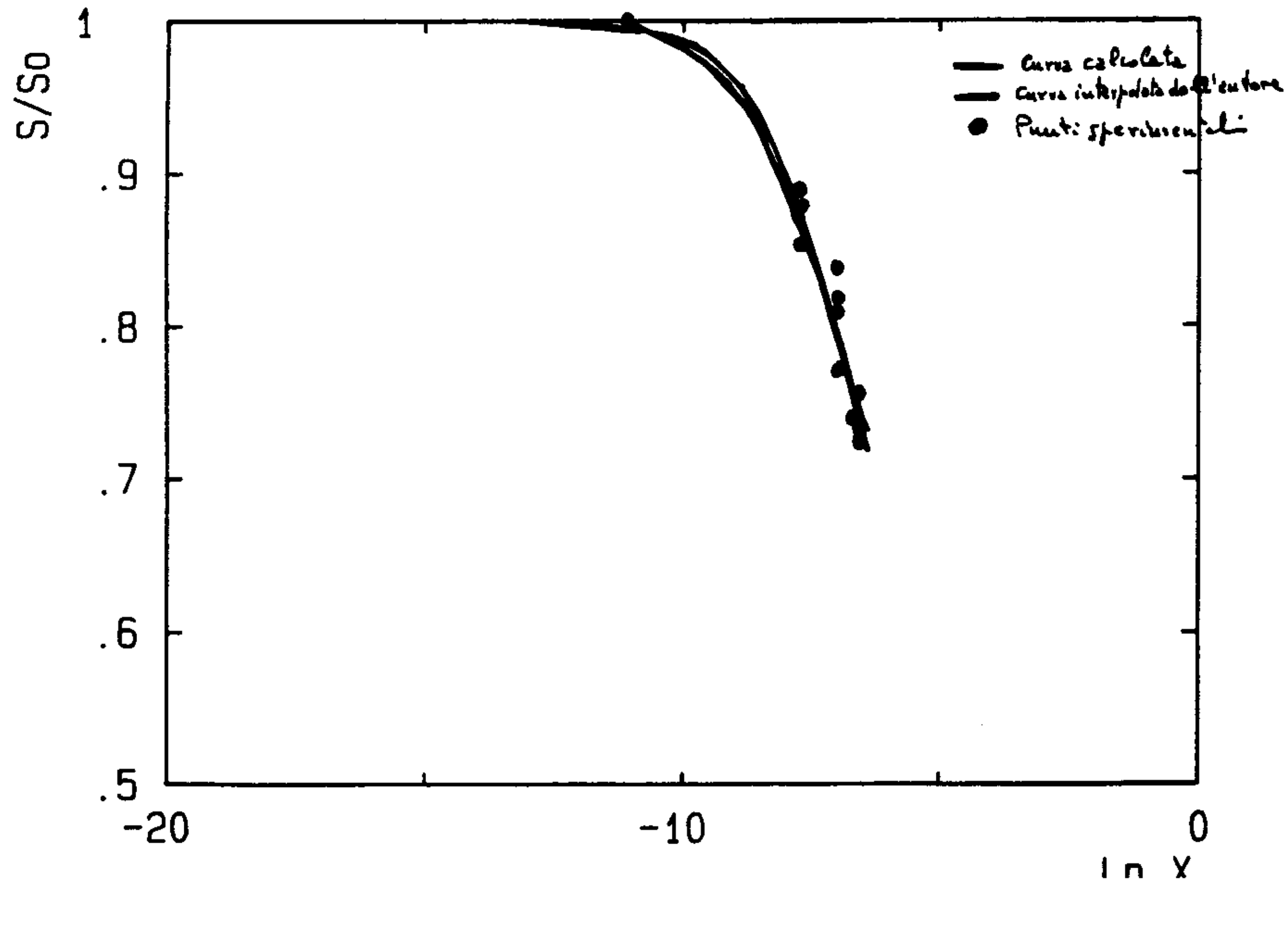
2) allows the evaluation of α, f, K from experimental data to be made.



ARGENTO-PASS.



Ferro Kasama exp.



An analysis of equation * shows that, being always $d\sigma / d\theta <= 0$, it is:

$$\alpha <= \frac{RT}{f\theta(1-f\theta)} = 4RT\ )\max$$

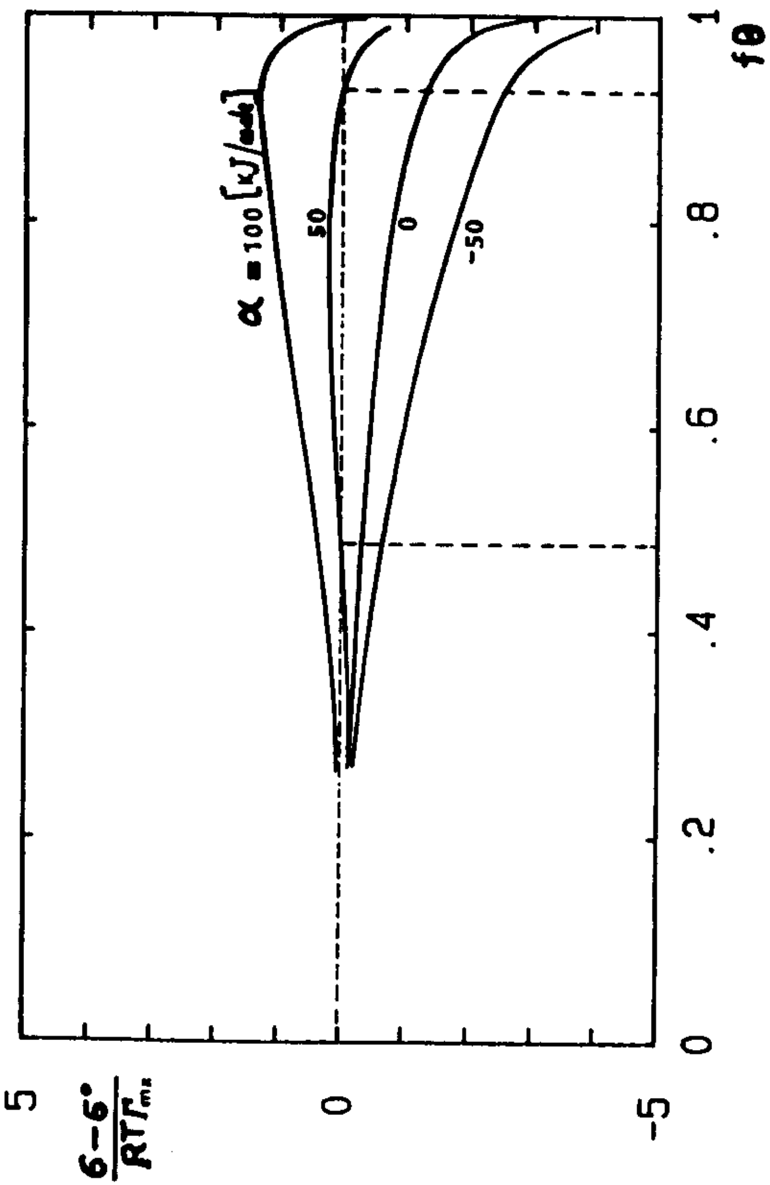
If $\alpha > 4RT$ then a surface miscibility gap is obtained between the values :

$$\frac{1}{2f}\left[1-\sqrt{1-\frac{4RT}{\alpha}}\right] <= \theta <= \frac{1}{2f}\left[1+\sqrt{1-\frac{4RT}{\alpha}}\right]$$

From experimental data, using a non linear fitting , values of α , f, K have been obtained:

System $\overset{+}{O}_2$	α kJ/mole	$-\frac{1}{2}z\varepsilon_{22}$ kJ/mole
Cu	57	497
Fe	21	496
Co	3	502
Ni	36	526
Ag	23	319

The table shows that the value of inter.parameter between oxygen atoms , is quite near to the value of the dissociation energy of oxygen : 493579 J/mol.



For values $X_{\Gamma max} < x < X_{sat}$ the model is not valid

because $\Gamma^1_{2,1} \neq \Gamma^1_2$

Beyond $X_{\Gamma max}$, the surface concentration is constant but

Up to Xsat , bulk concentration varies.

By integration of:

$$-RT\,\Gamma^1_{2,1} = \frac{d\sigma}{d\ln a_2} = -RT\left\{\Gamma^1_2 - \frac{X_2}{X_1}\Gamma^1_1\right\}$$

where $\Gamma_2 = \Gamma^1_{2max}$

$\Gamma^1_1 = \Gamma^1_{1max}$

we get the final formula:

$$\sigma = \sigma_{\Gamma max} + RT\,\Gamma^1_{2max}\ln\frac{X_{\Gamma max}}{X} + RT\,\Gamma^1_{2max}\frac{1-X_{sat}}{X_{sat}}\ln\frac{1-X_{\Gamma max}}{1-X}$$

This equation , written for X = Xsat ,

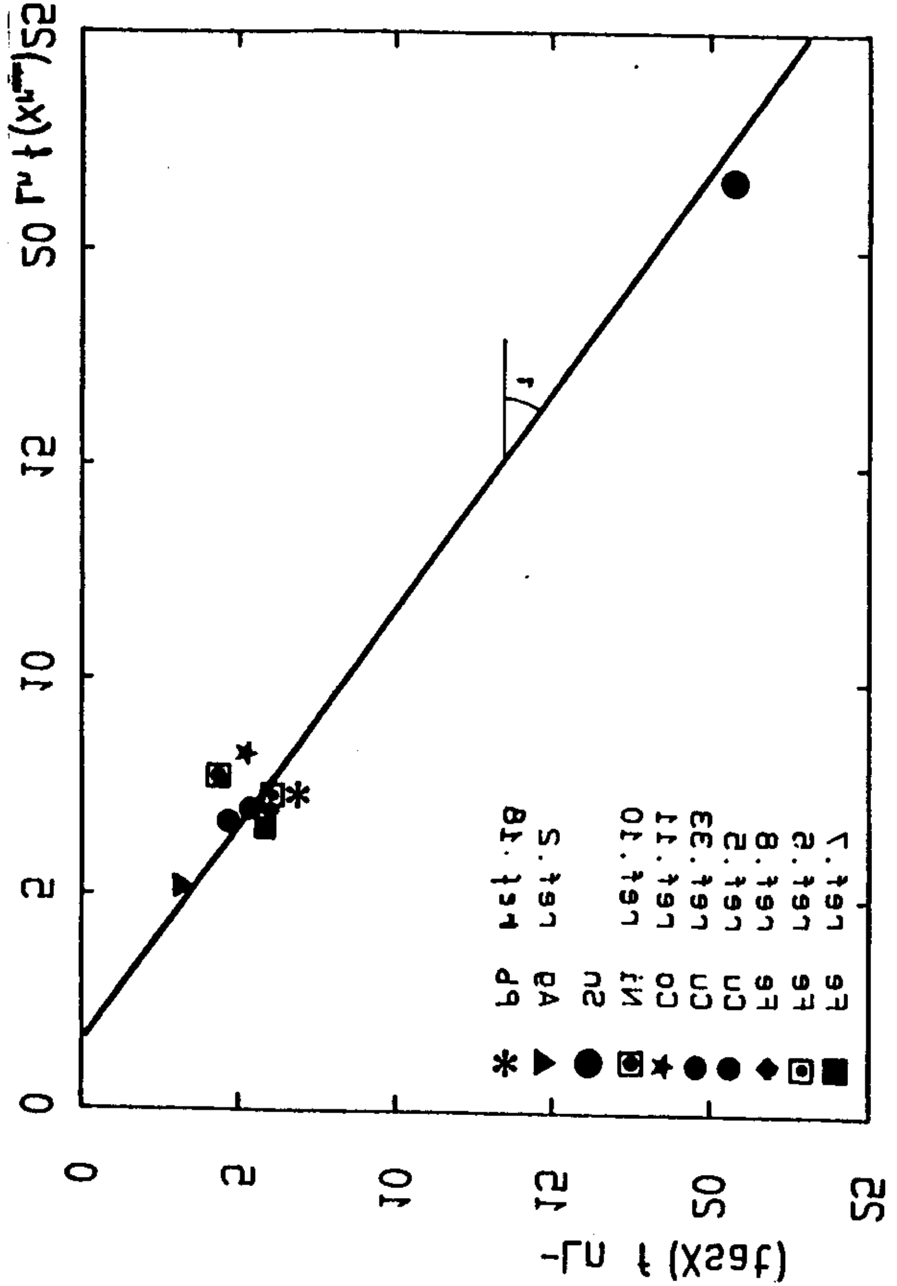
yields :

$$\ln\left[x_s(1-x_s)^{\frac{1-x_s}{x_s}}\right] = \ln\left[X_{\Gamma max}(1-X_{\Gamma max})^{\frac{1-x_s}{x_s}}\right] + \frac{\sigma_{\Gamma max}-\sigma_{sat}}{RT\,\Gamma^1_{max}}$$

that for X << 1 gives :

$$\mathrm{Ln}\,\frac{X_{sat}}{X_{\Gamma max}} = 3 + 0.5$$

This last formula allows an A PRIORI estimation of the composition necessary to reach the maximum value of oxygen surface coverage.



CONCLUSIONS

- INFLUENCE OF OXYGEN ON SURFACE TENSION OF PURE LIQUID METALS IN THE COMPOSITION RANGE

  $0 < X < X_{sat}$

- BEST FIT OF EXP. DATA UP TO X max WITH THE MODIFIED FOWLER GUGGENHEIM ISOTHERM
- ADSORPTION ENERGY DEPENDS ON BULK THERMODINAMIC PROPERT. AND , WHICH DEPENDS ON 'SURFACE COMPOS.'
- INTRODUCTION OF A 'SURFACE STRUCTURE COEFF.' TAKING INTO ACCOUNT THE STOICHIOMETRY OF ALL POSSIBLE OXIDES.
- THE MODEL SHOWS THAT :

  1) VERY SMALL VARIATIONS IN SURF. TENSION VALUES CAUSE CONSIDERABLE CHANGES IN THE VALUES.

  absolute need for much more accurate surf.tens. measurem. and for determinat. on a larger number of systems.

  2) SOME GENERAL RULES EXIST TO ESTIMATE X AND THE RELATIVE MAGNITUDE OF and FOR ALL METAL SYSTEMS.