

## Condensed Matter Physics Point defects.

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Vacancy



# Equilibrium vacancy concentration Gibbs potential

$$G(T,p) = U - TS - pV$$

n vacancy N atom

$$\triangle U = \epsilon_0 n$$

$$\triangle V = v_0 n$$

Entropy

$$S^{config} = k_B \ln \left( \begin{array}{c} N+n \\ n \end{array} \right) = k_B \ln \frac{(N+n)!}{N!n!}$$

Stirling-formula

 $\ln n! \approx n \ln n$ 

So

$$S^{config} = k_B \left[ (N+n) \ln(N+n) - N \ln N - n \ln n \right]$$

From this

$$\triangle G = \epsilon_0 n + p v_0 n - k_B T \left[ (N+n) \ln(N+n) - N \ln N - n \ln n \right]$$

Vacancy



Equilibrium concentration

$$\frac{\partial \bigtriangleup G}{\partial n} = 0$$

$$\epsilon_0 + pv_0 - k_B T[\ln(N+n) - \ln n] = 0$$

$$\frac{n}{N+n} = e^{-\frac{\epsilon_0 + \rho v_0}{k_B T}}$$

N >> n

$$n = Ne^{-\frac{\epsilon_0 + pv_0}{k_B T}}$$

Arrhenius plot (potassium)



#### Experimental determination

Thermal expansion

$$\frac{\bigtriangleup V}{V} \approx 3\frac{\bigtriangleup I}{I}$$
$$\bigtriangleup V = V_0 n$$

So

 $\triangle V = V_0 N \exp^{-\frac{\triangle H_V}{RT}}$ 

Resistivity

 $\triangle R \propto n$ 

Heat capacity at constant p.

$$c_{p} = \left(\frac{\partial H}{\partial T}\right)_{p}$$

Let us take

$$H=H_0+c_v\bigtriangleup H_v$$

where  $c_v$  is the vacancy

$$c_{\rho} = c_{\rho_0} + c_{\nu} \left( \frac{\partial \bigtriangleup H_{\nu}}{\partial T} \right)_{\rho} + \bigtriangleup H_{\nu} \left( \frac{\partial c_{\nu}}{\partial T} \right)_{\rho}$$

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$$c_{p} = c_{p_{0}} + c_{v} \left\{ \left( \frac{\partial \bigtriangleup H_{v}}{\partial T} \right)_{p} + \frac{\bigtriangleup H_{v}^{2}}{RT^{2}} \right\}$$

After neglecting the first term

$$\triangle c_{p} \approx \frac{c_{v_{0}}H_{v}^{2}}{RT^{2}}\exp^{-\frac{\triangle H_{v}}{RT}}$$

### Vacancy clusters



 $c_1$  mono  $c_2$  divacancy concentrations Rate equations

$$\frac{dc_1}{dt} = 2K_2c_2 - 2K_1c_1^2 - K_3c_1 \\ \frac{dc_2}{dt} = K_1c_1^2 - K_2c_2 - K_4c_2$$

$$K_1 \approx \nu_0 \exp^{-\frac{\triangle H_V}{RT}}$$

and

 $K_4 \approx 0$ 

then

$$K_1 c_1^2 - K_2 c_2 \approx 0$$

$$\frac{dc_1}{dt} = 2K_1 c_1^2 - 2K_1 c_1^2 - K_3 c_1$$

$$\frac{dc_1}{dt} = -K_3 c_1, \quad c(t) = c_0 \exp^{-K_3 t}$$

#### Phase rule



*P* is the number of phase *C* is the number of component *F* is the number of freedom The conditions for thermal equilibrium The thermal equilibrium in phases  $\alpha$  and beta

$$T_{\alpha} = T_{\beta}$$

The mechanical equilibrium

 $p_{\alpha} = p_{\beta}$ 

Chemical equilibrium between the *i*th component in phases  $\alpha$  and *beta* 

$$\mu_{i\alpha} = \mu_{i\beta}$$

Number of variables:

In each phase there are C - 1 composition variable, and T and Ep leading to

P(C + 1)



$$p_{\alpha} = p_{\beta} = p_{\gamma} = \dots P - 1$$
 equations

 $\mu_{1\alpha} = \mu_{1\beta} = \mu_{1\gamma} = \dots P - 1$  equations

$$\mu_{2\alpha} = \mu_{2\beta} = \mu_{2\gamma} = \dots P - 1$$
 equations

$$\mu_{C\alpha} = \mu_{C\beta} = \mu_{C\gamma} = \dots$$
 *P* - 1 equations

Number of equations

$$C(P-1) + 2(P-1) = (C+2)(P-1)$$

Gibbs phase rule

$$\begin{array}{rcl} P(C+1) & \geq & (C+2)(P-1) \\ \hline C+2 & \geq & P \end{array}$$

.



#### Binary systems



G(p, T) = U - TS + pV Gibbs free energy Sometime the F(T, V) == U - TS is used Since

$$dG - dF = \rho dV + V d\rho = \left(V + \rho \frac{\partial V}{\partial \rho_T}\right) d\rho + \frac{1}{V} \frac{\partial \rho}{\partial T_\rho} \rho V dT$$
$$= V \left(1 - \frac{V}{\kappa}\right) d\rho + \beta \rho V dT,$$

where  $\kappa$  is the isothermal compressibility and  $\beta$  the coefficient of thermal expansion, and dp = 0.

With more than one component

$$\mathrm{d}U = T\mathrm{d}S - \rho\mathrm{d}V + \mu_{A}\mathrm{d}N_{A} + \mu_{B}\mathrm{d}N_{B},$$

and

 $\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p + \mu_{A}\mathrm{d}N_{A} + \mu_{B}\mathrm{d}N_{B}.$ 

#### Binary systems



In this case

$$U = TS - \rho V + \mu_A N_A + \mu_B N_B.$$

and so

 $G = \mu_A N_A + \mu_B N_B.$ 

Let us introduce  $g = G/(N_{\rm A} + N_{\rm B})$ 

$$g=\mu_A c+\mu_B(1-c),$$

where  $c = \frac{N_{\rm A}}{N_{\rm A}+N_{\rm B}}$  is the concentration. One can find

$$\mathrm{d}g = -s\mathrm{d}T + \frac{1}{n}\mathrm{d}p + (\mu_A - \mu_B)\mathrm{d}c$$

where  $s = S/(N_{\rm A} + N_{\rm B})$  is the specific entropy and  $n = (N_{\rm A} + N_{\rm B})/V$ From this

$$\left(\frac{\partial g}{\partial c}\right)_{T,p}=\mu_{A}-\mu_{B}.$$



и<sub>в</sub>

*Figure:* Determination of the chemical potential in a binary system using the concentration dependence of the specific free enthalpy.

с





$$g_s = fg(c_1) + (1 - f)g(c_2).$$
  
$$c = fc_1 + (1 - f)c_2.$$

After eliminating f

$$g_{s} = \frac{c}{c_{1} - c_{2}}(g(c_{1}) - g(c_{2})) + \frac{c_{1}g(c_{1}) - c_{2}g(c_{2})}{c_{1} - c_{2}}$$

 $g_s$  as a function of the *c* concentration is a line that goes through the  $(c_1, g(c_1))$  and  $(c_2, g(c_2))$ 



Gibbs free energy curves with one (a) and two (b) minimums.

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*Figure:* Gibbs free energy of the liquid and the solid phase as a function of the concentration.

c<sub>s</sub>

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Figure: Simple phase diagram.

Volume fraction

 $c = fc_1 + (1-f)c_2$ 





Figure: Phase diagram of an eutectic material.