Lecture 18

Thermodynamics of Solutions

Measurement of Activity

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Today's Topics

- Measurement of activity
- Measurement of activity coefficient

Measurement of Activity

$$\sum_{K=1}^{C} X_k \, d\overline{Z}_k = 0$$ **Gibbs-Duhem Equation**

- For A-B binary solution

$$X_A \, d\overline{Z}_A + X_B \, d\overline{Z}_B = 0$$

- Using partial molar Gibbs free energy change for components in solution,

$$X_A \, d(\Delta\overline{G}_A) + X_B \, d(\Delta\overline{G}_B) = 0 \qquad \textbf{(6.33)}$$

- For a system of fixed composition, $dG = -SdT + VdP$
- At constant temperature, $dG_T = VdP_T$
- And for 1 mole of an ideal gas at constant temperature, using V = RT/P,

$$dG = (RT/P)\, dP = RT\,(dP/P) = RT \, d\ln P$$

- Hence the partial molar free energy of component k in solution will be

$$d\overline{G}_k = RT \, d\ln p_k$$

- For real solutions, replacing partial pressure with activity, we have

$$d\overline{G}_k = RT \, d\ln(p^0_k \cdot a_k) = RT \, d\ln a_k$$ *p^0_k is constant*

$$\mathbf{dG = RT\, d\ln a} \qquad \textbf{(6.38)}$$

$$dG = RT\, d\ln a$$

- Integrating at constant temperature from the standard state to any other state

$$G - G^0 = \Delta G = RT\ln a - RT\ln a^0$$

- By definition, the activity of a substance in its standard state is unity

$$G - G^0 = \Delta G = RT\ln a$$

- In terms of partial properties, similar integration of will give

$$\overline{G}_k - \overline{G}^0_k = \Delta\overline{G}_k = RT\ln a_k$$

$$d(\Delta\overline{G}_k) = RT\, d\ln a_k \qquad (6.40)$$

$$X_A\, d(\Delta\overline{G}_A) + X_B\, d(\Delta\overline{G}_B) = 0 \qquad d(\Delta\overline{G}_k) = RT\, d\ln a_k$$

$$X_A (RT\, d\ln a_A) + X_B (RT\, d\ln a_B) = 0$$

$$X_A\, d\ln a_A + X_B\, d\ln a_B = 0 \qquad (6.41)$$

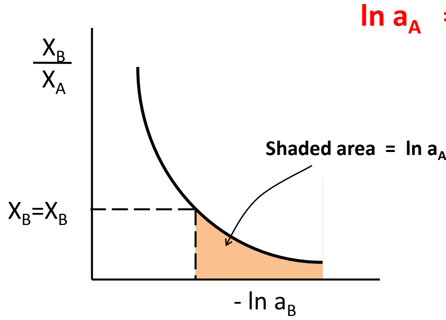
$$d\ln a_A = -\left(\frac{X_B}{X_A}\right) d\ln a_B$$

$$\int_{X_A=1}^{X_A=X_A} d\ln a_A = -\int_{X_A=1}^{X_A=X_A} \left(\frac{X_B}{X_A}\right) d\ln a_B$$

$$\ln a_A = -\int_{X_A=1}^{X_A=X_A} \left(\frac{X_B}{X_A}\right) d\ln a_B \qquad (6.42)$$

*The integration is done by graphical method using the plot **(X_B/X_A) vs. ln a_B***

$$\ln a_A = -\int_{X_A=1}^{X_A=X_A} \left(\frac{X_B}{X_A} \right) d \ln a_B$$



1. For $X_B \to 1$, $X_B/X_A \to \infty$ and $-\ln a_B = 0$.
   Curve exhibits a tail to plus infinity.

2. For $X_B \to 0$, $X_B/X_A \to 0$ and $-\ln a_B \to -\infty$
   Curve exhibits a tail to minus infinity.

Point 2 is important since the area under investigation includes a tails that extends to minus infinity.

This includes an uncertainty into the calculation.

Use of activity coefficient to measure activity

- For a binary A-B solution, $X_A + X_B = 1$

$$dX_A + dX_B = 0$$

$$X_A \left(\frac{dX_A}{X_A} \right) + X_B \left(\frac{dX_B}{X_B} \right) = 0$$

$$X_A \, d \ln X_A + X_B \, d \ln X_B = 0 \qquad (6.43)$$

$$X_A \, d \ln a_A + X_B \, d \ln a_B = 0 \qquad (6.41)$$

- Subtracting eq.(6.43) from eq.(6.41) gives

$$X_A \, d \ln \gamma_A + X_B \, d \ln \gamma_B = 0$$

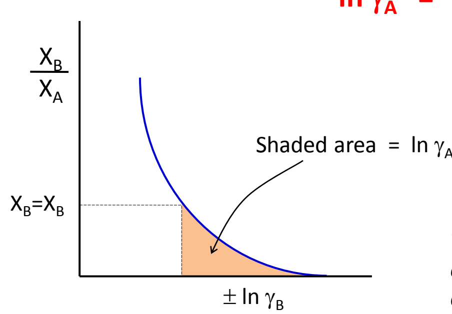
$$X_A \, d \ln \gamma_A + X_B \, d \ln \gamma_B = 0$$

$$d \ln \gamma_A = -\left(\frac{X_B}{X_A}\right) d \ln \gamma_B$$

$$\int_{X_A = 1}^{X_A = X_A} d \ln \gamma_A = -\int_{X_A = 1}^{X_A = X_A} \left(\frac{X_B}{X_A}\right) d \ln \gamma_B$$

$$\ln \gamma_A = -\int_{X_A = 1}^{X_A = X_A} \left(\frac{X_B}{X_A}\right) d \ln \gamma_B \qquad \textbf{(6.45)}$$

$$\ln \gamma_A = -\int_{X_A = 1}^{X_A = X_A} \left(\frac{X_B}{X_A}\right) d \ln \gamma_B$$



The sign of $\ln \gamma_B$ depends on positive or negative deviation of solution

1. For $X_B \to 1$, $X_B/X_A \to \infty$ and $\pm \ln \gamma_B = 0$.
Curve exhibits a tail to infinity.

2. Since the value of γ_B is always finite,
$\pm \ln \gamma_B$ will always has a finite value when $X_B/X_A \to 0$.

Example 6.5

The following data have been obtained for Cr-Ti solutions at 1250 °C.

X_{Cr}	0.09	0.19	0.27	0.37	0.47	0.67	0.78	0.89
a_{Cr}	0.302	0.532	0.660	0.788	0.820	0.863	0.863	0.906

Calculate the activity of titanium in a Cr-Ti solution containing 60 atom% Ti.

Answer

Integrating Gibbs-Duhem equation between the limits (1.0, 0.6) of titanium,

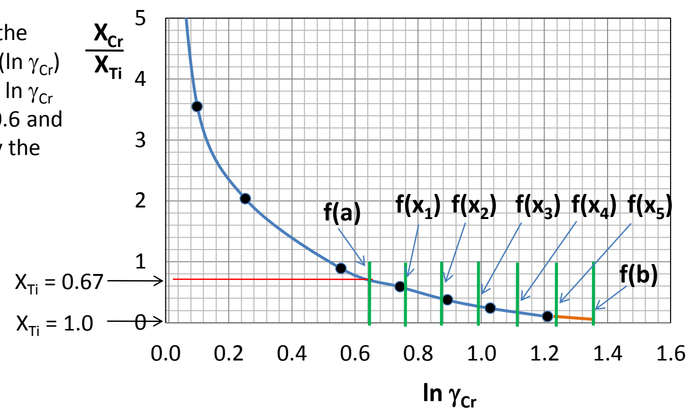
$$\ln \gamma_{Ti} = -\int_{X_{Ti}=1}^{X_{Ti}=0.6} \left(\frac{X_{Cr}}{X_{Ti}}\right) d\ln \gamma_{Cr} = +\int_{X_{Ti}=0.6}^{X_{Ti}=1} \left(\frac{X_{Cr}}{X_{Ti}}\right) d\ln \gamma_{Cr}$$

The integration will be done using graphical methods by using the plot (X_{Cr}/X_{Ti}) vs. $\ln \gamma_{Cr}$.

Data Sheet

X_{Cr}	X_{Ti}	X_{Cr}/X_{Ti}	a_{Cr}	γ_{Cr}	$\ln \gamma_{Cr}$
0.09	0.91	0.0989	0.302	3.355	1.210452
0.19	0.81	0.2346	0.532	2.8	1.029619
0.27	0.73	0.3699	0.66	2.444	0.893636
0.37	0.63	0.5873	0.778	2.103	0.743365
0.47	0.53	0.8868	0.82	1.745	0.556755
0.67	0.33	2.0303	0.863	1.288	0.253091
0.78	0.22	3.5454	0.863	1.106	0.10075
0.89	0.11	8.0909	0.906	1.018	0.01784

The area bounded by the curve and the axis for (ln γ_{Cr}) between the values of ln γ_{Cr} corresponding to X_{Ti}=0.6 and X_{Ti}=1.0 is calculated by the **trapezoidal rule**.



From the plot,
a = 0.64
b = 1.36

Let , n = 6
Cord width,
h = (b-a)/n = 0.12

The tail of the curve is extrapolated to zero value of (X_{Cr}/X_{Ti}).

a = 0.64	**x_1 = 0.76**	**x_2 = 0.88**	**x_3 = 1.00**
f(a) = 0.67	**f(x_1) = 0.58**	**f(x_2) = 0.38**	**f(x_3) = 0.28**
x_4 = 1.12	**x_5 = 1.24**	**b = 1.36**	
f(x_4) = 0.18	**f(x_5) = 0.08**	**f(b) = 0**	

The area under the curve

$$S = h\left(\frac{f(a) + f(b)}{2} + f(x_1) + f(x) + \ldots\ldots + f(x_{n-1})\right)$$

$$= (0.12)\ (0.67/2 + 0.58 + 0.38 + 0.28 + 0.18 + 0.08)$$

$$= 0.22$$

Then at X_{Ti} = 0.6,

$\ln \gamma_{Ti} = 0.22$ or, $\boldsymbol{\gamma_{Ti} = 1.25}$

Hence, the activity of Ti at X_{Ti} = 0.6,

$a_{Ti} = \gamma_{Ti} \cdot X_{Ti} = 1.25 \times 0.6 = \mathbf{0.75}$

Difficulties in measuring activity for solutions having a small amount of solutes

- Darken and Gurry introduce **α function** to determine activity when a solution contains small amount of solute X_A :

$$\alpha_k = \frac{\ln \gamma_k}{(1 - X_k)^2}$$

- The α function is always finite and well behaved by virtue of the fact that, as $X_k \rightarrow 1$, $\gamma_k \rightarrow 1$.

- For a binary A-B solution,

$$\alpha_A = \frac{\ln \gamma_A}{X_B^2} \quad \text{and} \quad \alpha_B = \frac{\ln \gamma_B}{X_A^2}$$

$$\alpha_B = \frac{\ln \gamma_B}{X_A^2}$$

$$\ln \gamma_B = \alpha_B X_A^2$$

$$d \ln \gamma_B = d(\alpha_B X_A^2) = 2 \alpha_B X_A \, dX_A + X_A^2 \, d\alpha_B$$

$$\ln \gamma_A = -\int_{X_A = 1}^{X_A = X_A} \left(\frac{X_B}{X_A} \right) d \ln \gamma_B$$

$$\ln \gamma_A = -\int_1^{X_A} (2\alpha_B X_B \, dX_A) - \int_1^{X_A} (X_A X_B \, d\alpha_B)$$

$$\ln \gamma_A = -\int_1^{X_A} (2\alpha_B X_B \, dX_A) - \int_1^{X_A} (X_A X_B \, d\alpha_B)$$

$$\int d(xy) = \int x\,dy + \int y dx$$

$$\int d(X_A X_B \alpha_B) = \int X_A X_B \, d\alpha_B + \int \alpha_B \, d(X_A X_B)$$

$$\int X_A X_B \, d\alpha_B = \int d(X_A X_B \alpha_B) - \int \alpha_B \, d(X_A X_B)$$

$$\int X_A X_B \, d\alpha_B = \int d(X_A X_B \alpha_B) - \int \alpha_B X_A \, dX_B - \int \alpha_B X_B \, dX_A$$

$$\ln \gamma_A = -\int_1^{X_A} (2\alpha_B X_B \, dX_A) - \int_1^{X_A} (X_A X_B \, d\alpha_B)$$

$$\int X_A X_B \, d\alpha_B = \int d(X_A X_B \alpha_B) - \int \alpha_B X_A \, dX_B - \int \alpha_B X_B \, dX_A$$

$$\ln \gamma_A = -\int_1^{X_A} 2\alpha_B X_B \, dX_A - \int_1^{X_A} d(X_A X_B \alpha_B) + \int_1^{X_A} \alpha_B X_A \, dX_B + \int_1^{X_A} \alpha_B X_B \, dX_A$$

$$\ln \gamma_A = -\int_1^{X_A} 2\alpha_B X_B \, dX_A - \int_1^{X_A} d(X_A X_B \alpha_B) - \int_1^{X_A} \alpha_B X_A \, dX_A + \int_1^{X_A} \alpha_B X_B \, dX_A$$

$$\ln \gamma_A = -\int_1^{X_A} 2\alpha_B X_B \, dX_A - \int_1^{X_A} d(X_A X_B \alpha_B) - \int_1^{X_A} \alpha_B X_A \, dX_A + \int_1^{X_A} \alpha_B X_B \, dX_A$$

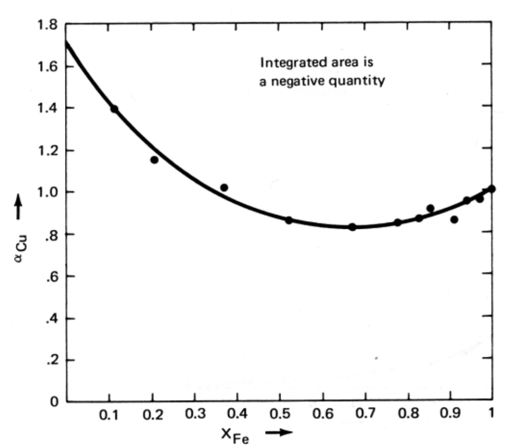
$$\ln \gamma_A = -\int_1^{X_A} d(X_A X_B \alpha_B) - \int_1^{X_A} \alpha_B (X_A + X_B) \, dX_A$$

$$\ln \gamma_A = -X_A X_B \alpha_B - \int_1^{X_A} \alpha_B \, dX_A$$

As α_B is everywhere finite, this integration does not involve α tail to infinity.

When α_B is plotted against X_A, the area under the curve from X_A=X_A to X_A=1 equals the right hand side of the above equation.

Then, ln γ_A at X_A=X_A is obtained as ($-a_B X_A X_B$) minus the area under the curve.



The variation of α_{Cu} with composition in iron-copper solution

Next Class

Lecture 19

Thermodynamics of Solutions

Dilute Solutions and Multicomponent Systems