Tutorial problems and questions

1. Show that it condnesed systems $H \approx E$.

Answer

The change in enthalpy due to a change in pressure from P_1 to P_2 is given by (See 1) $\Delta H = \int_{P_1}^{P_2} V_m(1-\alpha T)dP$ where α is the isobaric coefficient of thermal expansion and V_m is the molar volume.

Typically, most of materials are considered at 1 atmospheric pressure (which is a very small quantity by itself). Further, since the coefficient of expansion for condensed systems (liquids and solids) is very small, the total change in enthalpy due to pressure changes is very small. Hence, it can be neglected.

As an example, consider iron, for which $V_m = 7.1 cm^3$, $\alpha = 0.3 \times 10^{-4} K^{-1}$. Even an increase of pressure from 1 to 100 atmospheres at 298 K thus increases the enthalpy by about 70 J or so, which can be achieved just by increasing temperature by about 3 K.

2. Derive $S^{mix}_{config} = RT\left\{(1-x_B)\ln(1-x_B) + x_B \ln x_B\right\}$

Answer

$S_{config} = k_B \ln \omega$ where ω is the number of available states.

In the case of pure materials, there is only one state and hence $S_{config} = 0$, On the other hand, for N_A and N_B atoms of types A and B respectively places on a lattice of N_{Avo} sites,

$$\omega = \frac{N_A! N_B!}{N_{Avo}!}$$

Thus, $S^{mix}_{config} = k_B \ln\left[\frac{N_A! N_B!}{N_{Avo}!}\right]$

We can use Stirling's approximation which is valid for large $\ln n! = n \ln n - n$, and which states n.

Thus, $S^{mix}_{config} = k_B[N_A \ln N_A - N_A + N_B \ln N_B - N_B - N_{Avo} \ln N_{Avo} + N_{Avo}]$

But, . $N_{Avo} = N_A + N_B$

Hence,
$S^{mix}_{config} = k_B N_{Avo}[(N_A/N_{Avo})\ln N_A + (N_B/N_{Avo})\ln N_B - ((N_A + N_B)/N_{Avo})\ln N_{Avo}]$
where we have also multiplied and divided the qualtity in the square brackets by N_{Avo}.

$$S^{mix}_{config} = k_B N_{Avo}[(N_A/N_{Avo})\ln(N_A/N_{Avo}) + (N_B/N_{Avo})\ln(N_B/N_{Avo})]$$

$$S^{mix}_{config} = R[(1-x_B)\ln(1-x_B) + x_B \ln x_B].$$