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Variation of chemical potential with T and P

👤 Urmi Roy · 🕒 Oct 23, 2013

Oct 23, 2013

🔗 #1

U

Urmi Roy 👤

💬 :754

👍 : 1



So the expression for Gibb's free energy is:

$$dG = -SdT + VdP + \mu dN,$$

Here, we see that the **Gibb's free energy changes with temperature (dT), change in pressure (dP) and change in chemical potential** (as a result of change in particle number).

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My question is: we know chemical potential varies with both change in temperature and pressure. So if we don't add/remove particles from the system, the chemical potential *does* change with variation of P and T...**so is that already included in the above equation?**

(That is, in the above equation, are we accounting for the change in Gibb's free energy as a result of change in chemical potential as a result of variation of T and P, in addition to the change in chemical potential due to change in particle number).

Further, when the number of particles changes, there **might be a number of chemical reactions that take place, so the temperature T might change because of that also, which would change the sdT term at the beginning, right?**


I guess I'm just having problems understanding chemical potential :-/


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Oct 23, 2013

 #2
**Chestermiller**
 Mentor

 :18,647

 : 3,600

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Urmi Roy said: 

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The answer to all your questions is "yes", the equation for dG takes all these things into account. The Gibbs Free Energy G can be expressed as a function of T , P , and N_1, \dots, N_m , where m is the number of species in the solution:

$$G = G(T, P, N_1, \dots, N_m)$$

An infinitesimal change in G can be represented using the chain rule for partial differentiation:

$$dG = \frac{\partial G}{\partial T} dT + \frac{\partial G}{\partial P} dP + \frac{\partial G}{\partial N_1} dN_1 + \dots + \frac{\partial G}{\partial N_m} dN_m$$

Each of the partial derivatives in this equation is a function of T, P, and the N's, with

$$\frac{\partial G}{\partial T} = -S$$

$$\frac{\partial G}{\partial P} = V$$

and

$$\frac{\partial G}{\partial N_i} = \mu_i$$

I hope this helps.

Oct 25, 2013

#3

D

DrDu

Science Advisor

:5,959

: 718

Of course μ is a function of T and P, also.

Given that $\mu = \partial G / \partial N$ we have

$$(\partial \mu / \partial T)_P = \partial^2 G / \partial N \partial T = \partial^2 G / \partial T \partial N = -(\partial S / \partial N)_P = S_m$$

i.e. the partial molar entropy and

analogously

$$(\partial \mu / \partial P)_T = V_m \text{ the partial molar volume.}$$

So for fixed N,


$$d\mu = -S_m dT + V_m dP$$

pallab

Nov 22, 2013

 #4

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Urmi Roy  :754 : 1

Can I just go on to ask what the difference between chemical potential and chemical affinity is? They seem to , intuitively, mean the same thing but chemical potential is +ve for a reaction that's progressing and affinity is negative!


Also, is A (affinity) always the same sign as the rate of reaction?

Nov 24, 2013

 #5

D

DrDu

 Science Advisor :5,959 : 718

$$A = -\Delta G_r = -\sum \nu_i \mu_i$$
where ν_i are the stoichiometric coefficients of the reaction taking place.

So basically A is a weighed sum of chemical potentials.

1 person

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