

## The effect of gravitational field on thermodynamics of ideal-dilute solutions

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Received: 01-August-2022, Manuscript No. PCAIJ-22-001; Editor assigned: 03-August -2022, PreQC No. PCAIJ-22-001 (PQ); Reviewed: 17-August -2022, QC No. PCAIJ-22-001; Revised: 22-August -2022, Manuscript No. PCAIJ-22-001 (R); Published: 29-August -2022, DOI: 10.37532/pcaij.2022.17 (4).001

### Abstract

It's customary in physical chemistry textbooks to neglect the effect of gravity on thermodynamic properties. But is it always an accurate procedure? In this paper we have tried to obtain gravitational corrections to internal energy, entropy, enthalpy, Gibbs free energy and molecular distribution for nonelectrolyte ideal-dilute solutions. We have shown these corrections to be approximately  $E_{cor} \approx \frac{g^2 D^2}{12RT} \sum_i n_i M_i^2$ ,  $S_{cor} \approx \frac{g^2 D^2}{24RT^2} \sum_i n_i M_i^2$  (and similar equations for G and H). Finally, some rules are suggested for deciding whether it is necessary to consider the effect of gravity.

**Keywords:** gravitational field, ideal-dilute solutions, equilibrium thermodynamics, chemical

### Introduction

The effect of gravitational field on thermodynamic properties of simple solutions is often neglected due to the relatively small gravitational acceleration. However, these effects can be more significant when dealing with systems in stronger fields. For instance, in an ultracentrifuge, the artificial gravity generates a density gradient which is the basis for separation of biomolecules such as DNA molecules, proteins, etc. This density gradient is due to the particular distribution of solute particles in the gravitational field. We discuss this distribution in the next section.

In some cases, even neglecting the minimal effects due to gravity can lead to a contradiction to laws of thermodynamics, specially the second law. Secrest [7] explained that how a non-rigorous treatment of these effects would wrongly predict the existence of "an osmotic perpetual motion machine".

We consider the behavior of nonelectrolyte solute molecules in such a gravitational field. Then we'll derive the difference in thermodynamic properties that arises when the influence of gravity is taken into account. We make following assumptions in order to make calculations easier:

The solvent is completely incompressible. Furthermore, dissolving more solute would not change the solution's volume. In a mathematical point of view, we say  $(\frac{\partial V}{\partial n_i})_{P,T,n_{j \neq i}}$

Our system (the solution) is in thermodynamic equilibrium.

**Citation:** Aryan T. The effect of gravitational field on thermodynamics of ideal-dilute solutions. *Phys Chem Ind J.* 2022.17 (4).001.

the solution is assumed to be an "ideal-dilute" one; namely, 'solute molecules interact essentially only with solvent molecules'. [4]

As mentioned earlier, we only deal with solutions of nonelectrolytes.

The gravitational field, temperature and density do not vary from point to point through the system.

The geometrical shape of the container is a prism parallel to the direction of the field. D and A are the height of the prism and the area of the base, respectively. Therefore, its volume is  $V=AD$

**The distribution of solute molecules**

Consider a specific solute species  $i$  present in the system. Invoking the chemical equilibrium condition, for any arbitrary transfer of this species between phases (different heights), we have

$$dw_{non-pv} = \sum_{\alpha} \mu_i^{\alpha} dn_i^{\alpha}$$

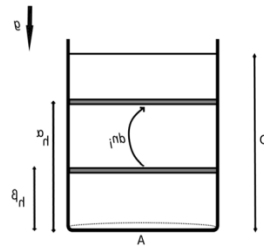
Where the sum goes over different phases (heights) and  $dw_{non-pv}$  is any work done except the expansion work (also known as 'PV work') in the process of transfer. In this case the  $w_{non-pv}$  is due to gravitational work. (Eq.1 can be easily obtained using the equations

$$dE = TdS - \sum_{\alpha} P_{\alpha} dV_{\alpha} + \sum_{\alpha} \mu_i^{\alpha} dn_i^{\alpha} \text{ And } dE = dq + (dw_{pv} + dw_{non-pv}) = TdS - \sum_{\alpha} P_{\alpha} dV_{\alpha} + dw_{non-pv}$$

For two arbitrary heights (say  $h_{\alpha}$  and  $h_{\beta}$ ; see Fig.1) this equation becomes

$$\begin{aligned} dw_{non-pv} &= \mu_i^{\alpha} (dn_i) + \mu_i^{\beta} (-dn_i) \\ &= (\mu_i^{\alpha} - \mu_i^{\beta}) dn_i \end{aligned}$$

**Fig 1. Transfer of  $dn_i$  moles of substance  $i$  between two arbitrary heights**



Because gravitational force is conservative, we can write

$$dw_{gr} = -dE_{p_{gr}} = -g(h^{\beta} - h^{\alpha})dm_i = M_i g(h^{\beta} - h^{\alpha})dn_i$$

Where  $M_i$  is the molar mass of  $i$ . Substituting this into Eq.2 and cancel the  $dn_i$  factor on both sides, we obtain

$$M_i g(h^{\beta} - h^{\alpha}) = (\mu_i^{\alpha} - \mu_i^{\beta})$$

Since the solution is assumed to be ideal-dilute, chemical potential of  $i$  is obtained from

$$\mu_i = \mu_i^0 + RT \ln \frac{c_i}{c_0} \quad c_0 \equiv 1 \text{ mol L}^{-1}$$

If we substitute Eq.5 into Eq.4, we obtain

$$M_i g(h^{\beta} - h^{\alpha}) = \mu_i^0(P_{\alpha}, T) - \mu_i^0(P_{\beta}, T) + RT \ln \frac{c_i^{\alpha}}{c_i^{\beta}}$$

Now we show that  $\mu_i^0(P_{\alpha}, T)$  and  $\mu_i^0(P_{\beta}, T)$  are equal. In other words, in this case,  $\mu_i^0$  is independent of pressure

$$\frac{\partial \mu_i}{\partial P} = \frac{\partial \left( \frac{\partial G}{\partial n_i} \right)}{\partial P} = \frac{\partial \left( \frac{\partial G}{\partial P} \right)}{\partial n_i} = \frac{\partial V}{\partial n_i}$$

And since it is assumed  $\frac{\partial V}{\partial n_i} = 0$  (assumption No.1), it leads to  $\frac{\partial \mu_i}{\partial P} = 0$  and so  $\mu_i^0(P_{\alpha}, T) = \mu_i^0(P_{\beta}, T)$ . Therefore, we can cancel the first two terms on the right side of Eq.6 to get

$$M_i g(h^\beta - h^\alpha) = RT \ln \frac{c_i^\alpha}{c_i^\beta}$$

Note the similarity between Eq.9 and Boltzmann distribution law. We can interpret this result using a microscopic point of view. The energy of an individual molecule of  $i$  can be written as

$$\varepsilon = \varepsilon_{tr} + \varepsilon_{rot} + \varepsilon_{vib} + \varepsilon_{el} + \varepsilon_{int} + \varepsilon_{gr} \quad (10)$$

Where the first four terms are translational, rotational, vibrational and electronic energies, respectively.  $\varepsilon_{int}$  is the energy due to interaction with solvent. The last term is the gravitational potential energy, which is equal to  $mgh$ .

Since temperature is constant through the solution (assumption No.5), the first four terms do not vary from point to point. Furthermore,  $\mu$  and  $\varepsilon_{int}$ —as a result—interaction with solvent do not depend on the pressure. So  $\varepsilon_{int}$  is also constant. So we have

$$\Delta\varepsilon = \Delta\varepsilon_{gr} = mg\Delta h$$

And invoking Boltzmann distribution law for molecular energy distribution, we obtain

$$\frac{n_i^\beta}{n_i^\alpha} = \frac{c_i^\beta}{c_i^\alpha} = e^{\frac{-m_i g(h^\beta - h^\alpha)}{k_B T}} = e^{\frac{-M_i g(h^\beta - h^\alpha)}{RT}}$$

Which is consistent with Eq.9. we can rewrite this result in form of

$$c_i^\alpha = a e^{\frac{-M_i g h^\alpha}{RT}}$$

Where  $a$  is a constant that should be determined using the normalization condition

$$\begin{aligned} n_{i,tot} &= \int c_i^\alpha dV^\alpha = \int_{h=0}^{h=D} (a e^{\frac{-M_i g h}{RT}}) (A dh) \\ n_{i,tot} &= A a \left( \frac{-RT}{M_i g} \right) \left( e^{\frac{-M_i g D}{RT}} - 1 \right) \\ &= A D a \left( \frac{-RT}{M_i g D} \right) \left( e^{\frac{-M_i g D}{RT}} - 1 \right) \end{aligned}$$

We now define  $X_i$  by  $X_i \equiv \frac{-M_i g D}{RT}$ . Using this definition and  $V=AD$ , we find

$$n_{i,tot} = \frac{aV}{X_i} (e^{X_i} - 1)$$

Substituting  $a$  from Eq.16 into Eq.13, we get

$$c_i^\alpha = a e^{\frac{-M_i g h^\alpha}{RT}} = \left[ \frac{n_{i,tot}}{V} \left( \frac{X_i}{e^{X_i} - 1} \right) \right] e^{\frac{-M_i g h^\alpha}{RT}}$$

Finally, we have derived the distribution of solute molecules which plays a key role in deriving other properties of the system.

### The change in internal energy (E)

In this section, we find the energy difference between these two cases; one in which a gravitational field is present and a solution with no external fields acting on it. We call these cases 'simplified' and 'real' cases, respectively. This difference arises because of the work of gravitational field in the process of moving from the 'simplified' to the 'real' case.

$$\begin{aligned} \Delta E &= E_{real} - E_{simp} = w_{gr,simp \rightarrow real} = -\Delta E p_{gr} = -(E p_{real} - E p_{simp}) \\ E p_{real} &= \int g h^\alpha dm_i^\alpha = \int g h^\alpha M_i dn_i^\alpha = \int_{h=0}^{h=D} (g h M_i c_i) (A dh) \end{aligned}$$

When we substitute Eq.17 into the last equation, we obtain

$$E p_{real} = M_i g A a \int_{h=0}^{h=D} h e^{\frac{-M_i g h}{RT}} dh$$

$$= M_i g A a \left( \frac{RT}{M_i g} \right)^2 [e^{X_i}(X_i - 1) + 1]$$

$$E_{p_{real}} = n_{i,tot} RT \left[ 1 - \frac{X_i e^{X_i}}{e^{X_i} - 1} \right]$$

On the other hand, when the distribution of particles through the solution is even (and it's not affected by the gravity yet), we have  $c_i^\alpha = \frac{n_{i,tot}}{V} = \frac{n_{i,tot}}{AD}$  (for all heights) and therefore

$$E_{p_{real}} = \int_{h=0}^{h=D} (ghM_i c_i)(Adh) = \frac{n_{i,tot} M_i g D}{2} = n_{i,tot} RT (-X_i/2)$$

Eventually, we substitute Eq.21 and Eq.22 into Eq.18 to obtain

$$\Delta E = n_{i,tot} RT \left[ \frac{X_i e^{X_i}}{e^{X_i} - 1} - \frac{X_i}{2} - 1 \right]$$

If we had several species instead of one, we could just add individual terms to obtain the desired result. So general form of  $\Delta E$  for several species becomes

$$\Delta E = \sum_i n_{i,tot} RT \left[ \frac{X_i e^{X_i}}{e^{X_i} - 1} - \frac{X_i}{2} - 1 \right]$$

### The change in entropy

We shall start with the equation below

$$dE = TdS - \sum_\alpha P_\alpha dV_\alpha + \sum_\alpha \mu_i^\alpha dn_i^\alpha$$

Since the solution is incompressible the second term vanishes. Also for similar reasons we obtained Eq.9 from Eq.4, we could simplify  $\mu_i = \mu_i^0 + RT \ln \frac{c_i}{c_0}$  to  $RT \ln \frac{c_i}{c_0}$ . We should integrate Eq.25 from simplified case to the real one. So

$$\Delta E = T\Delta S + \int_{case1}^{case2} \sum_\alpha RT \ln \frac{c_i^\alpha}{c_0} dn_i^\alpha = T\Delta S + \int_{case1}^{case2} \sum_\alpha RT V_\alpha \ln \frac{c_i^\alpha}{c_0} dc_i^\alpha = T\Delta S + \sum_\alpha RT V_\alpha \int_{c_i^\alpha = n_{i,tot}/V}^{c_i^\alpha = c_i^\alpha} \ln \frac{c_i^\alpha}{c_0} dc_i^\alpha$$

$$\Delta E = T\Delta S + RT \sum_\alpha V_\alpha \left[ \frac{c_i^\alpha}{c_0} \left( \ln \left( \frac{c_i^\alpha}{c_0} \right) - 1 \right) - \frac{n_{i,tot}}{V} \ln \left( \frac{n_{i,tot}}{V} - 1 \right) \right]$$

This sum goes over all heights; therefore, it's actually an integral. Substituting  $V_\alpha = Adh$  and Eq.17 into Eq.27, we find

$$\Delta E = T\Delta S + RTA \int_{h=0}^{h=D} dh \left[ \frac{ae^{-\frac{M_i g h^\alpha}{RT}}}{c_0} \left( \ln \left( \frac{ae^{-\frac{M_i g h^\alpha}{RT}}}{c_0} \right) - 1 \right) - \frac{n_{i,tot}}{V} \ln \left( \frac{n_{i,tot}}{V} - 1 \right) \right]$$

Using a number of standard integrals, the final result of this scary integral leads to

$$\Delta E = T\Delta S + n_{i,tot} RT \left[ \frac{X_i e^{X_i}}{e^{X_i} - 1} - \ln \left( \frac{e^{X_i} - 1}{X_i} \right) - 1 \right]$$

If we substitute Eq.23 into this equation, we finally get

$$\Delta S = S_{real} - S_{simp} = n_{i,tot} R \left[ \ln \left( \frac{e^{X_i} - 1}{X_i} \right) - \frac{X_i}{2} \right]$$

And similar to  $\Delta E$ , we can generalize this result to several species

$$\Delta S = \sum_i n_{i,tot} R \left[ \ln \left( \frac{e^{X_i} - 1}{X_i} \right) - \frac{X_i}{2} \right]$$

### The change in enthalpy and Gibbs free energy

This time, we start with definition of enthalpy ( $H=E + PV$ ). So

$$\Delta H = \Delta E + \int_{case1}^{case2} \sum_{\alpha} dP_{\alpha} V_{\alpha} = \Delta E + \int_{case1}^{case2} \sum_{\alpha} V_{\alpha} dP_{\alpha} = \Delta E + \sum_{\alpha} V_{\alpha} \int_{case1}^{case2} dP_{\alpha}$$

$\int_{case1}^{case2} dP_{\alpha}$  For each phase (height) could be estimated by famous equation  $\Delta P = \rho gh$  (we've already assumed that  $\rho$  is constant through the system; so we can use this equation). Therefore

$$\Delta H = \Delta E + \rho g \sum_{\alpha} A h^{\alpha} dh^{\alpha} = \Delta E + \rho g \int_{h=0}^{h=D} A h dh$$

$$\Delta H = \Delta E + \rho g V D / 2 = \sum_i n_{i,tot} RT \left[ \frac{X_i e^{X_i}}{e^{X_i} - 1} - \frac{X_i}{2} - 1 \right] + \rho g V D / 2$$

Finally,  $\Delta G$  is the easiest part

$$\Delta G = \Delta H - T \Delta S = \sum_i n_{i,tot} RT \left[ \frac{X_i e^{X_i}}{e^{X_i} - 1} - \ln \left( \frac{e^{X_i} - 1}{X_i} \right) - 1 \right] + \rho g V D / 2$$

### Limiting equations

Usually  $X$  is so small (as we see in next section) that we can neglect second terms and higher in the Taylor expansion of equations for  $E$ ,  $S$ ,  $H$  and  $G$ . If we do so (we can handle this expansion using a computational program or website as Wolfram Alpha) we get

$$\Delta E \approx \sum_i \frac{n_{i,tot} RT}{12} (X_i)^2 = \frac{g^2 D^2}{12 RT} \sum_i n_{i,tot} M_i^2$$

$$\Delta E \approx \sum_i \frac{n_{i,tot} RT}{12} (X_i)^2 = \frac{g^2 D^2}{12 RT} \sum_i n_{i,tot} M_i^2$$

$$\Delta E \approx \sum_i \frac{n_{i,tot} RT}{12} (X_i)^2 = \frac{g^2 D^2}{12 RT} \sum_i n_{i,tot} M_i^2 \cdot 9$$

$$\Delta E \approx \sum_i \frac{n_{i,tot} RT}{12} (X_i)^2 = \frac{g^2 D^2}{12 RT} \sum_i n_{i,tot} M_i^2$$

### Numerical case

Now, we evaluate equations of last section in a real situation. Consider 1L of saturated aqueous solution of sucrose in 250C. This solution approximately contains 6.05 mole of sucrose. Molar mass of sucrose equals to 342.3 g mol<sup>-1</sup> and density of solution is 1.33 g cm<sup>-3</sup> [1]. If we let height of container ( $D$ ) be 20cm, then we find

$$X = \frac{-MgD}{RT} = -2.7 \times 10^{-4}$$

Substituting  $X$  into four limiting equations, we have

$$\Delta E \approx 9.0 \times 10^{-5} J, \Delta S \approx 1.5 \times 10^{-7} Jk^{-1}$$

$$\Delta H \approx 1.3 J, \Delta G \approx 1.3 J$$

It turns out that corrections to  $G$  and  $H$  are more significant compared to  $E$  and  $S$ . But why is this so? This happened as a result of the contribution of the 'PV' term in  $H$  and  $G$ . (please note that  $H = E + PV$  and  $G = E - TS + PV$ ). Nevertheless, these corrections are still so small that can be neglected in many thermodynamic studies. However, based on four limiting equations, we can see these deviations could be more important in some cases, such as

When temperature is too low (because  $T$  appears in the dominator of correction terms). Unfortunately, as temperature goes to zero, quantum mechanical effects become more important and so our treatment loses its accuracy (for instance, see [5] for a treatment of low-temperature thermodynamic system). Our procedure can just predict that the deviations would be significant as  $T$  goes to zero, however,

we cannot compute these deviations with the desired accuracy.

When molar masses of particles are so high. (for example Nanoparticle colloids or biomolecules solutions)

When gravitational field is so strong. (for instance, an ultracentrifuge may generate a gravitational field of 1000000g)

When the system is so lengthy in the direction parallel to the field. (That is, D is high, for Example Ocean and lakes)

When solution's density is high. (especially in case of Gibbs free energy and enthalpy; this is because of the contribution of the term  $\frac{\rho g V D}{2}$  to equations 38 and 39)

Otherwise, we may neglect minor gravity effects, safely.

## CONCLUSION

We have derived equations for calculating gravitational corrections to thermodynamic properties in ideal-dilute solutions. These equations can be used for a more rigorous treatment of ideal-dilute solutions, but for most of purposes, they found to be negligible in normal conditions as already expected. Then we have shown briefly when it's safe to neglect gravity effects and in which cases it's better to use caution in dealing with these deviations. After all, please note that we have assumed that the solution is completely incompressible; If compressibility of fluids is taken to account, the effect of gravity is much more significant than what we estimated.

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