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Comparison of the Approximate Solutions for Free Neutral Atoms

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THE method of Thomas-Fermi treats the atomic electron as a gas at zero temperature, obeying Fermi-Dirac statistics. This leads to the equation[1]

$$\frac{d^2\Phi}{dx^2}=x^{-\frac{1}{2}}\Phi^{\frac{3}{2}}. \tag{1}$$

The boundary conditions for neutral atoms are

$$\begin{aligned}\Phi&=1 \quad \text{for} \quad x=0\\ \Phi&\rightarrow 0 \quad \text{for} \quad x\rightarrow\infty.\end{aligned} \tag{2}$$

The comparison of the different approximate solutions of the Thomas-Fermi equation would be facilitated if there existed a measure for the approximation degree of any approximate solution. For this measure Umeda[2] has proposed the numerical value of the variational integral

$$I(\Phi)=\int_0^\infty[(\Phi')^2+\tfrac{4}{5}\Phi^{5/2}/x^{1/2}]dx, \tag{3}$$

evaluated by putting the given approximate solution in place of Φ. For Miranda's[3] exact solution, direct numerical quadrature of (3) gives the value

$$I=1.3625, \tag{4}$$

which should of course be the limiting minimum value of I. Since the minimization of I is equivalent to the integration of the Thomas-Fermi equation, the better approximate solution should result in the smaller numerical value of I. The general formula,

$$\Phi=\frac{1}{(1+ax)^\alpha}; \quad \alpha>\tfrac{1}{5} \tag{5}$$

is now being studied on the basis of the approximation degree (private communication of Professor K. Umeda) previously mentioned. If we take[4] $\alpha=2$, $\alpha=7/5$, and $\alpha=9/5$, we obtain

$$\alpha=2;\begin{cases}I=1.3663\\ a=0.569272\end{cases} \quad \alpha=7/5;\begin{cases}I=1.3636\\ a=0.881206\end{cases} \tag{6}$$

$$\alpha=9/5;\begin{cases}I=1.3650\\ a=0.645996.\end{cases}$$

Comparing the values to the standard value $I=1.3625$ we see that the formula for $\alpha=2$, $\alpha=7/5$, and $\alpha=9/5$ is of fairly high approximation degree. Table I gives a comparison of the various approximations, *viz*, Baker[5] approximation Φ_{Ba}, Sommerfeld[6] approximation Φ_{So}, Buch-Caldwell-Fermi[7] approximation $\Phi_{Fe,Bu}$, and our approximation $_{I}\Phi_{Ti}$ for $\alpha=2$; $_{II}\Phi_{Ti}$ for $\alpha=7/5$ and $_{III}\Phi_{Ti}$ for $\alpha=9/5$. We have limited the values to three significant decimal places, which are sufficient for our purposes.

TABLE I.

x	$\Phi_{Fe,Bu}$	Φ_{So}	Φ_{Ba}	$_{I}\Phi_{Ti}$	$_{II}\Phi_{Ti}$	$_{III}\Phi_{Ti}$
0.01	0.985	0.969	0.985	0.991	0.988	0.989
0.03	0.959	0.931	0.959	0.968	0.970	0.966
0.08	0.902	0.860	0.902	0.915	0.909	0.913
0.1	0.882	0.836	0.882	0.895	0.888	0.893
0.2	0.793	0.741	0.793	0.806	0.797	0.804
0.3	0.721	0.667	0.720	0.729	0.721	0.726
0.4	0.660	0.607	0.659	0.663	0.655	0.661
0.5	0.607	0.556	0.606	0.605	0.600	0.604
0.6	0.562	0.514	0.561	0.555	0.553	0.555
0.9	0.453	0.412		0.437	0.442	0.438
1.0	0.425	0.385		0.407	0.413	0.408
1.4	0.333	0.302		0.310	0.327	0.313
1.8	0.268	0.244		0.245	0.265	0.251
2.0	0.244	0.221		0.219	0.241	0.225
2.5	0.194	0.176		0.170	0.196	0.177
3.0	0.157	0.143		0.137	0.163	0.144
4.0	0.108	0.099		0.0931	0.121	0.101
4.5	0.093	0.084		0.0788	0.106	0.0863
5.0	0.079	0.073		0.0676	0.0942	0.0746
10.0	0.024	0.023		0.0223	0.0410	0.0269
20.0	0.0058	0.0056		0.00652	0.0167	0.00874

From Table I we see that the well-known Sommerfeld asymptotic formula is not a better approximation. It has a sufficient foundation in regard to the asymptotic behavior, while the March[8] formula is obviously an improved approximate solution. The Sommerfeld approximation is relatively complicated. More details will be published elsewhere.

In conclusion the writer wishes to thank Professor Dr. Kwei Umeda for friendly private comments.

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Electron Theory of Metals and Hydrogen Overvoltage

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IT was recently pointed out[1] that differences in hydrogen overvoltage, η, from one metal to another for given electrolysis conditions primarily depend on the heat, $D(M-H)$, of adsorption of atomic hydrogen. The η–$D(M-H)$ relationship is approximately linear. Other quantities such as work function, lattice constant, etc., have been considered in the comparison of overvoltages for different metals. It is shown below that these observations can be correlated to the $\eta-D(M-H)$ relationahip.

The heat of adsorption of atomic hydrogen can be calculated by[2]

$$D(M-H)=\tfrac{1}{2}\{D(M-H)+D(H-H)\}+23.06(X_M-X_H)^2, \tag{1}$$

where D's are the bond energies and X's the electronegativities. Characteristics of the metal appear in $D(M-M)$ and X_M. The latter is approximately 0.355ϕ, ϕ being the work function of the metal.[3,4] Furthermore, $D(M-M)$ can be computed from the heat of sublimation L of the metal, and L can be correlated to parameters characterizing the metal. Thus, $L\approx 3\phi/5$ for the alkali metals, copper, silver, and gold[5] and $D(M-H)$ depends on ϕ. The relationship between L and ϕ for other metals is more involved, but the simple equation $L\approx 3\phi/5$ suffices to indicate a trend. The $\eta-\phi$ dependence observed by Bockris[6] can thus be accounted for qualitatively; L and consequently $D(M$–$H)$ increases with ϕ, and since η decreases with increasing values of $D(M-H)$, the overvoltage decreases with increasing work function.

The energy of sublimation L for Na, K, etc., is proportional[5] to the power $\frac{2}{3}$ of the free electron density, and consequently an increase in electron density in the electrode causes a decrease in overvoltage. This conclusion is verified experimentally.[7] Conversely, large lattice constants and large compressibilities correspond to relatively low electron densities and high overvoltages.

Another approach in correlating overvoltage to electrode material can be followed by applying the expression for ϕ derived by Wigner and Bardeen.[8] The expression contains the cohesive energy of the metal, and consequently the bond energy $D(M-H)$ can be expressed in terms of the work function. Still another approach would be to apply Mulliken's treatment of charge-transfer-no-bond adsorption.[9,10]

These various treatments show that hydrogen overvoltage (or exchange current) can be correlated to various quantities characterizing the electrode material. However, the resulting relationships would probably be more complicated than the

$\eta - D(M-H)$ dependence which follows more directly from the kinetic treatment. A detailed treatment will be published.

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* Postdoctoral fellow, 1953–54, on a project sponsored by the Office of Naval Research.

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On the Entropy of Mixing of Liquid Solutions

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MANY binary mixtures of polyatomic nonpolar molecules with approximately central field of forces show an important excess entropy [Table I (B)], which at first may be attributed to the following causes:

(*1*) *Order-disorder effect.*—This leads to a negative, and practically negligible excess entropy.[1,2]

(*2*) *Changes in the rotational* (*or orientational*) *partition function on mixing.*—The contributions of this effect to Ts_e and to g_e are of the same order of magnitude and of the same sign.[3]

(*3*) *Effect of the change in the motion of molecules around their equilibrium position.*—The corresponding excess entropy is mainly related to the volume change on mixing.[4–6]

Let us consider in more detail the excess entropy resulting from this effect and calculated by the cell model assuming an intermolecular potential independent of orientation. We also assume that

$$\epsilon_{AB}^{*2} = \epsilon_{AA}^{*}\epsilon_{BB}^{*} \quad r_{AB}^{*} = (r_{AA}^{*} + r_{BB}^{*})/2, \tag{1}$$

where ϵ_{ij}^{*} and r_{ij}^{*} are coordinates of the minimum of the curve describing the interaction between molecules i and j as function of their distance apart. Experimental data on second-virial coefficient of mixtures of simple gases[7] and even of complicated polyatomic molecules[8] justify the use of (1).

For a *solution composed of molecules of the same size* ($r_{AA}^{*} = r_{BB}^{*}$, but $\epsilon_{AA}^{*} \neq \epsilon_{BB}^{*}$), Ts_e is of opposite sign to, and of the order of 10 percent to 50 percent of g_e; at zero pressure $v_e < 0$, $Ts_e < 0$, $g_e > 0$.[4,6] For a *solution composed of molecules of different size* ($r_{AA}^{*} \neq r_{BB}^{*}$, and $\epsilon_{AA}^{*} \neq \epsilon_{BB}^{*}$), for sufficiently large differences in diameters, when $|(r_{BB}^{*} - r_{AA}^{*})/r_{AA}^{*}| > \frac{1}{2}|(\epsilon_{BB}^{*} - \epsilon_{AA}^{*})/\epsilon_{AA}^{*}|$ both the excess volume and excess entropy became positive.[5,6]

The aforementioned conclusions are valid when $\epsilon_{AB}^{*} \approx (\epsilon_{AA}^{*} + \epsilon_{BB}^{*})/2$, as is the case for homopolar solutions as long as (1) is valid.

It is to be noticed, that the structure of a solution of molecules of the same size is very similar to that of pure liquids, the order-disorder effects being small; while the structure of a solution of molecules of different size can no longer be considered as identical to that of the pure liquids.

It has not as yet been possible to draw definite conclusions as to the origin of the excess entropy, since experimental data on the excess entropy of mixtures of molecules of similar size were lacking.

We have measured the heat of mixing of one such system, namely CCl_4+neopentane at 0°C. As the vapor pressure and the excess volume of CCl_4+neopentane at 0°C were already measured in our laboratory,[9] all the excess properties of this system are at present known. The heat of mixing is for a mole fraction 0.5, 75 ± 5 cal/mole^{-1}.[10]

The experimental excess properties of mixtures of globular molecules and the parameters of the central force field, estimated from critical ratio, virial coefficients, heats of vaporization, densities, and viscosities, are given in Table I. The comparison of these data lead to following conclusions:

The excess entropy seems to depend rather strongly on the excess volume: for the four mixtures of molecules with $v_e > 0$, $Ts_e > 0$, and $Ts_e \approx g_e$, whereas for the mixture CCl_4+neopentane with $v_e < 0$, we obtained a very small and probably negative value of Ts_e and $Ts_e \ll g_e$.

The sign and the relation between the excess properties and their dependence upon the intermolecular forces are, for all systems studied, correctly predicted by the cell theory assuming (1) and a central force law. The observed negative entropy (-1 ± 8

Table I.

A. Solution of molecules of the same size, $|(r_{BB}^{*} - r_{AA}^{*})/r_{AA}^{*}| \ll |(\epsilon_{BB}^{*} - \epsilon_{AA}^{*})/\epsilon_{AA}^{*}|$.

$AA+BB$	$(\epsilon_{BB}^{*} - \epsilon_{AA}^{*})/\epsilon_{AA}^{*}$	$(r_{BB}^{*} - r_{AA}^{*})/r_{AA}^{*}$	v_e cm^{3}mole^{-1}	Ts_e cal mole^{-1} for a mole fraction 0.5	g_e
neopentane +cyclohexane[a]	0.30	0.00	−1.0		+44
$CO+CH_4$[b]	0.44	+0.04	−0.3		+28
neopentane +CCl_4[a,c]	0.30	−0.04	−0.5	−1	+76
neopentane +benzene[a]	0.32	−0.08	−0.5		+135

B. Solutions of molecules of different size, $|(r_{BB}^{*} - r_{AA}^{*})/r_{AA}^{*}| > \frac{1}{2}|(\epsilon_{BB}^{*} - \epsilon_{AA}^{*})/\epsilon_{AA}^{*}|$.

$AA+BB$	$(\epsilon_{BB}^{*} - \epsilon_{AA}^{*})/\epsilon_{AA}^{*}$	$(r_{BB}^{*} - r_{AA}^{*})/r_{AA}^{*}$	v_e cm^{3}mole^{-1}	Ts_e cal mole^{-1} for a mole fraction 0.5	g_e
$SiCl_4+CCl_4$[d]	0.07	−0.04	+0.015	+13	+20
CCl_4+benzene[e,f]	0.02	−0.04	+0.01	+7	+19
cyclohexane +benzene[f,g]	0.02	−0.08	+0.65	+115	+76
cyclohexane +CCl_4[f,h]	0.00	−0.04	+0.16	+20	+17

[a] See reference 9.
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