being the intrinsic chemical potential and ϕ the potential energy per unit mass of the long range gravitational or electrostatic forces. I also showed that, in considering the work done in transferring a particle from one point A in the system to another point B , Melehy had neglected the contribution to the work done in changing the volume occupied by the particle from that at A to that at B .

In a further communication⁴, Melehy has applied his theory to obtain a formula for the current-voltage relation at a p - n junction. His formula undoubtedly gives good agreement with the experimental results quoted. His reply to my criticism of his theories, however, consists of the statement that his theory does account for the work contribution mentioned earlier. He gives two reasons for this, the first that it is accounted for in the "subtle arguments" used in developing his theory, the second that his formula gives good agreement with the experimental results used. Both reasons clearly do not assist scientific discussion, especially as in his arguments he postulates an expression for the diffusion force (see equation (28) of ref. 1).

No comment is made on my defence of the constancy of the chemical potential at equilibrium, which is basically important because his theory is explicitly based on a contradiction of this well known result.

In section (6) of ref. 2 the following statement is made: "The conclusion that $d\mu \neq 0$ whenever $dP \neq 0$ in the two preceding examples is an inevitable consequence of equation (16)

$$\{d\mu = -sdT + (1/n)dP\}$$

It might be of historical interest to state that the example of an atmosphere in thermal equilibrium happens to have been treated by Gibbs²¹, who also has concluded that for that case $d\mu \neq 0$ in thermal equilibrium. Clearly, it may now be stated that, under thermal equilibrium conditions, $d\mu$ will never vanish in any system wherever $dP \neq 0$; that is wherever $dn \neq 0$.

On further study of ref. 2, and taking into account especially this passage and the two examples cited, it is certain that the principal error has been a confusion between what Gibbs⁹ called the intrinsic chemical potential and the chemical potential of a system under long range forces, which, for electric forces, is known as the electro-chemical potential. It is, of course, well known that this latter quantity $\mu_i + \phi$ is a constant everywhere at equilibrium and that its constancy determines the lining up of Fermi-levels. It is also well known (see, for example, ref. 3) that in a quasi-static isothermal displacement δr of a mass element m the work done is

$$\begin{aligned}\delta W &= \delta r \cdot \{\nabla(Pv) + \nabla\phi\}m \\ &= \delta r \cdot \{\nabla(Pv) - \nabla\mu_i\}m \\ &= -m\delta r \cdot \nabla f_i\end{aligned}\quad (1)$$

where μ_i , f_i are the intrinsic chemical potential and intrinsic Helmholtz free energy per unit mass.

Thus at equilibrium

$$\nabla\mu_i = -\nabla\phi \quad (2)$$

and $-\nabla\mu_i$ may in some way be regarded as a fictional force balancing that caused by the long-range forces. The work done in a quasi-static isothermal displacement, however, is not solely that arising from these forces, but is given by (1). If ∇f_i is regarded also as a fictional force, it is, of course, irrotational.

A further confusion occurs in section (8) of ref. 2 concerning the thermodynamic pressure and the pressure obtained from the Virial theorem in liquids and vapours. It is claimed that in liquids if P is calculated by the Virial theorem it could be magnitudes higher than in the vapour. This is wrong, as reference to any good text (for example, Hirschfelder, Curtiss and Bird⁶) on liquid theory would show; in fact the pressures according to either kinetic theory or thermodynamics are the same,

and this does not conflict, as implied, with the fact that, in the classical case, Maxwell-Boltzmann statistics applied.

The agreement with experiment of the formula obtained by Melehy for the current-voltage relation of a p - n junction is interesting and this communication is written in the hope that a valid explanation may be made of the new terms introduced in the formula.

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CHEMISTRY

Simplification of the Synthesis of Tetramethyldipicrylamine

BECAUSE the antibacterial agent, tetramethyldipicrylamine, which we reported recently¹ has aroused wide interest we have developed a modification in the synthesis of the intermediate, 3,3',5,5'-tetramethyldiphenylamine, which will make it possible for research workers to prepare experimental quantities of pure material in good yield without the necessity of elaborate equipment. The methods reported previously involved heating 3,5-dimethylaniline and its hydrochloride in either a glass² or metal³ autoclave at 235°–250° C or heating a mixture of 3,5-dimethylaniline and 3,5-dimethylphenol at 300°–400° C under 50 to 300 atmospheres pressure⁴.

It was found that a sealed tube reaction was feasible when a slurry of equal amounts of 3,5-dimethylaniline and its hydrochloride, not exceeding a total of 7 g, was packed into a glass tube by means of a glass wool plug. The tube, selected to have a volume of 3 ml/g of material, was sealed and heated in a constant temperature oven for 72 h at 230°–240° C. A 74 per cent yield of good quality 3,3',5,5'-tetramethyldiphenylamine was obtained. This was washed with warm 7 per cent hydrochloric acid, extracted with either benzene or ether, dried over anhydrous sodium sulphate and nitrated without further purification to give a 72 per cent yield of the antibacterial agent, tetramethyldipicrylamine, melting point 232° C dec., reported: 231° C dec. We have extended the use of this simplified sealed tube method to the synthesis of 3,3'-dimethyldiphenylamine in 64 per cent yield and to 3,3' bis- and 3,3',5,5'-tetrakis-trifluoromethyldiphenylamine in lesser yields.

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