

the disaccharide, relative to D-glucose, on paper chromatography in solvent systems (a) and (b) was 0.53, and was indistinguishable from the disaccharide isolated from the *S. newington* LPS.

Acknowledgements. We are indebted to Professor Bengt Lindberg for his interest and to the *Swedish Natural Science Research Council* for financial support.

- Hellerqvist, C. G., Lindberg, B. and Lönngren, J. *Acta Chem. Scand.* **25** (1971) 939.
- Lönngren, J. *Unpublished results.*
- Gorin, P. A. J. and Perlin, A. S. *Can. J. Chem.* **39** (1961) 2474.
- Bredereck, H., Wagner, A., Faber, G., Ott, H. and Rauther, J. *Chem. Ber.* **92** (1959) 1135.
- Hakomori, S. *J. Biochem. (Tokyo)* **55** (1964) 205.
- Björndal, H., Hellerqvist, C. G., Lindberg, B. and Svensson, S. *Angew. Chem.* **9** (1970) 610.
- Sawadeker, J. S., Sloneker, J. H. and Jeanes, A. R. *Anal. Chem.* **12** (1965) 1602.
- Hellerqvist, C. G., Larm, O. and Lindberg, B. *Acta Chem. Scand.* **25** (1971) 743.
- Wolfrom, M. L. and Thompson, A. *Methods in Carbohydrate Chemistry* **2** (1963) 211.

Received March 10, 1971.

On the Concept of "Mechanochemical Equilibrium"

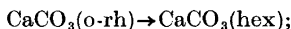
KARL-GUSTAV STRID

Department of Physics, Chalmers University of Technology, S-402 20 Gothenburg 5, Sweden

In a study of the grinding of aragonite, $\text{CaCO}_3(\text{o-rh})$, and calcite, $\text{CaCO}_3(\text{hex})$, Schrader and Hoffmann¹ discovered the enantiotropic phase transition



Normally, the transition between these allotropes of calcium carbonate is monotropic:



$$\Delta G(25^\circ\text{C}) = -7.42 \times 10^5 \text{ J kmol}^{-1} \quad (\text{II})$$

According to Schrader and Hoffmann, "the established phase equilibrium between calcite and aragonite ... does not, of course, correspond to thermodynamical equilibrium". These authors proposed the concept of "mechanochemical equilibrium".

Moreover, Schrader and Hoffmann found that the distribution of calcium carbonate between the two phases was determined by the type of mill used in the experiment.

The purpose of the present paper is to show that no further equilibrium concept need be introduced in order to account for the phase equilibrium (I).

The dependence of chemical potential on particle size. Textbooks of physical chemistry usually define the chemical activity of a pure solid as unity, irrespective of the state of the solid surface. However, due to surface tension, the activity of any condensed body depends on the curvature of the surface of the body.

Suppose that the chemical potential of a condensed phase with a flat surface (*i.e.* a surface of infinite radius of curvature) and the equilibrium vapour pressure outside it are G_∞ and P_∞ , respectively. The chemical potential for any other value, r , of the radius of curvature is then

$$G(r) = G_\infty + RT \ln [P(r)/P_\infty] \quad (1)$$

where R is the molar Boltzmann constant,* T is temperature, $P(r)$ is the actual vapour pressure, and activity factors have been neglected.

An energetical consideration of a spherical droplet in phase equilibrium with its vapour (see, *e.g.*, Wannier²) yields, for constant T ,

$$\ln [P(r)/P_\infty] = 2\gamma V/RT r \quad (2)$$

γ being the surface tension of the interface between the condensed phase and its vapour, V the molar volume of the vapour species in the condensed phase, and r being positive for a convex and negative for a concave surface. Putting (2) into (1) yields

$$G(r) = G_\infty + (2\gamma V/r) \quad (3)$$

The condition for phase equilibrium. Since G depends on the size of the condensed-phase particles, the enantiotropic phase transition (I) may be treated like any other phase equilibrium, the equilibrium criterion being that G be equal in the two phases. The concept of mechanochemical

* Since R , the "molar gas constant", is not specifically related to gases, the author would prefer the name "molar Boltzmann constant".

equilibrium then becomes unnecessary and confusing.

Two solid phases, A and B, ground to particles of radius r_A and r_B , respectively, may coexist in phase equilibrium if

$$G_{A\infty} + (2\gamma_A V/r_A) = G_{B\infty} + (2\gamma_B V/r_B) \quad (4)$$

provided that (2) is valid.

If experimentally determined equilibrium values of $1/r_B$ are plotted against the corresponding values of $1/r_A$, a straight line should come out. Extrapolation of the plot to $1/r_A = 0$ (or $1/r_B = 0$), ($G_{A\infty} - G_{B\infty}$) and V being known from other experiments, should yield values for γ_A and γ_B .

A numerical estimate. To estimate the magnitude of the contribution $2\gamma V/r$ to the chemical potential, one must know the surface tension γ . For solid sodium chloride and solid magnesium oxide one calculates, from the experimental results of Nicolson,³ $\gamma = 0.4 \text{ N m}^{-1}$ and $\gamma = 2-4 \text{ N m}^{-1}$, respectively, in agreement with measurements of the surface enthalpy of these substances (for a discussion see Tosi⁴). Aragonite and calcite being somewhat harder than sodium chloride but not as hard as magnesium oxide (hardness⁵ of aragonite 3.5-4, calcite 3, halite 2.5, periclase 5.5 on the Mohs scale), it seems reasonable to put $\gamma = 1 \text{ N m}^{-1}$ for the former solids.

Assuming the vapour phase to consist of carbon dioxide, one calculates for aragonite (density⁵ 2950 kg m^{-3} , molar mass 84.1 kg kmol^{-1}) $V = 2.85 \times 10^{-2} \text{ m}^3 \text{ kmol}^{-1}$, and thus

$$G(r) - G_\infty \approx \frac{0.06 \text{ J kmol}^{-1} \text{ m}}{r}$$

Inserting $r = 10^{-7} \text{ m}$ (0.1 μm) one finds $G(r) - G_\infty \approx 6 \times 10^6 \text{ J kmol}^{-1}$, i.e. of the same order of magnitude as ΔG of reaction (II). Thus, for aragonite and calcite ground to fine particles, the phase equilibrium (I) may come out as a case of energetical equilibrium.

Acknowledgement. The author wishes to thank Dr. Stig Johansson, Industrial Laboratories, Swedish Match Company, Jönköping, for stimulating discussions on the concept of chemical equilibrium.

- Schrader, R. and Hoffmann, B. *Z. Chemie* **6** (1966) 388.
- Wannier, G. H. *Statistical Physics*, John Wiley & Sons, New York 1966, p. 148.

- Nicolson, M. M. *Proc. Roy. Soc. London Ser. A* **228** (1955) 490, p. 507.
- Tosi, M. P. *Solid State Phys.* **16** (1964) 1, p. 92.
- Handbook of Chemistry and Physics*, Ed., R. C. Weast, 49th Ed., The Chemical Rubber Co., Cleveland, Ohio 1968, p. B-302.

Received March, 11, 1971.

The Reaction of Benzoyldurene with Methylmagnesium Bromide and *t*-Butylmagnesium Chloride

INGOLF CROSSLAND and TORKIL HOLM

Department of Organic Chemistry, Technical University of Denmark, DK-2800 Lyngby, Denmark

The reactions of benzoyldurene with methylmagnesium and *t*-butylmagnesium halides have been studied by Fuson *et al.*¹⁻³ (see review⁴) and by the present authors.⁵ Previous uncertainty¹⁻⁴ regarding the nature of the primary reaction products has now been clarified by the observation that the Grignard-benzophenone adducts on protonation produce rather labile enols (I and IV, dur=2,3,5,6-tetramethylphenyl) (*cf.* Experimental). Prototropic rearrangements, and other reactions of the latter, give rise to the secondary products which were partly identified by Fuson *et al.*¹⁻³ NMR data (*cf.* Experimental) support the structures

