

Our experiments have consisted of the equilibration of samples of Johnson Matthey "Specpure" nickel monoxide and iron sesquioxide at 500 and 700°C for periods of one week at 1 kbar oxygen pressure. The high pressure oxidation equipment was as previously described [9] and the materials were analysed for metal concentration, the presence of oxidising valencies and by X-ray diffraction before and after equilibration with oxygen. In no experiment was the oxygen content of the oxides after equilibration found to be in excess of the expected stoichiometric concentrations, and the X-ray data revealed no structures other than NiO and Fe₂O₃.

For nickel monoxide in particular the present result is more acceptable than the previously suggested oxygen excess of 0.07, since excess oxygen concentrations of only 0.006 in CoO at 950°C and 0.04 in FeO at 600°C correspond to the oxygen-rich phase boundary of the monoxides [9, 10]. If the defect interaction energies [9, 11] in FeO, CoO and NiO represent the important parameters involved in bringing about phase-transition in the monoxides, then the maximum permitted oxygen excess in the three

oxides on the oxygen-rich phase-boundary should decrease in the order FeO > CoO > NiO, and in the case of nickel monoxide only be attained at very high oxygen pressures at these temperatures.

References

1. C. C. ADDISON, B. F. G. JOHNSON, and N. LOGAN, *J. Chem. Soc.* (1965) 4490.
2. R. ROY, *Bull. Soc. Chim.* (1965) 1065.
3. D. P. BOGATSKY, *Zhur. obshchei Khim.* **21** (1951) 3.
4. D. P. BOGATSKY and V. MINEYEVA, *Fiz. Tverd. Tela. Akad. nauk SSSR Sbornic Statei* **2** (1959) 361.
5. D. P. BOGATSKY and V. MINEYEVA, *Zhur. obshchei Khim.* **29** (1959) 1358.
6. A. N. KUZNETSOV, *Zhur. neorg. Khim.* **13** (1968) 2077.
7. C. S. HOLTERMANN, *Ann. Chim* **14** (1940) 122.
8. S. P. MITOFF, *J. Chem. Phys.* **35** (1961) 882.
9. J. T. COX and C. M. QUINN, *J. Mater. Sci.* **4** (1969) 33.
10. A. MUAN, *Amer. J. Sci.* **256** (1958) 171.
11. J. S. ANDERSON, *Proc. Roy. Soc. A* **185** (1946) 69.

Received 28 September

and accepted 14 October, 1970

R. W. DRAKEFORD*

C. M. QUINN†

*Inorganic Chemistry Laboratory
The University of Oxford, UK*

On the Measurement of the Surface Energy of Solids

In *J. Mater. Sci.* **5** (1970) 351 a paper on the bubble technique for the measurement of the surface energy of solids was published. The theory of the measurement and equation 4 used for calculating surface energy γ from the observations is easily shown to be erroneous. It assumes that the high-pressure gas present in the bubbles causes no strain and no stress in the surrounding metal. This assumption cannot be accepted.

(1) In many instances "the bubbles were faceted" that is, the gas-solid interface was plane. No capillary pressure acts across plane interfaces. Hence, in these experiments, the whole gas pressure was balanced by the compression stresses in the solid. Nevertheless, some values for γ were deduced from these observations also.

(2) In some similar systems, "swelling and warping" takes place. It is not stated whether

any such deformation was noticed in the irradiated copper. If a deformation was present, the stresses caused by it counteracted the pressure in the bubbles. If the deformation was negligible, that is the external volume of the solid did not change in spite of the formation of bubbles in it, then the solid material was under a compressive stress, and this stress acted against the gas pressure.

The surface energy of solids cannot be determined by the bubble technique as it cannot by any other method so far devised [1, 2].

References

1. J. J. BIKERMAN, *Phys. Stat. Sol.* **10** (1965) 3; **12** (1965) K 127.
2. *Idem*, "Physical Surfaces" (Academic Press, New York, 1970), p. 202.

Received 30 July

and accepted 14 October 1970 J. J. BIKERMAN
15810 Van Aken Blvd.
Cleveland, Ohio 44120, USA

*Now with Urquhart-Dykes and Lord, Columbia House, 69 Aldwych, London, EC2.

†Now at Department of Physical Chemistry, The University, Birmingham.