

UNITS AND NOTATION

Some explanation of policy on the matter of units and notation is particularly desirable in a volume of this type at this point in history, owing to the current debates and changes concerning SI units, and, to a lesser extent, concerning n.m.r. conventions. The problems of introducing SI do not, fortunately, impinge very greatly on n.m.r. since all the important measurable parameters of a spectrum — chemical shifts, coupling constants, and relaxation times — do not differ in the old and the new systems. However, attempts to express those parameters in terms of more fundamental quantities (*i.e.* to evaluate them theoretically) do lead to difficulties and, in particular, to changes in equations. The research literature is still largely non-SI, and the decision was taken for the current volume that each Reporter should be free to use the system of his choice provided there is self-consistency *within each chapter*. Thus Chapter 1 uses mainly SI equations (except where explicitly stated otherwise) whereas Chapter 2 basically uses non-SI expressions.

Such individual freedom seems appropriate at the present time; more uniformity may be justifiable for the future. Some particular points may, perhaps, be noted here:

- (i) As has been mentioned in the Foreword, Dr. Raynes discusses in Chapter 1 the current controversy regarding the appropriate signs to be used for chemical shifts.
- (ii) Magnetic susceptibilities differ by a factor of 4π in SI and c.g.s. systems because of the effects of rationalization. Thus

$$\chi_{\text{SI}} = 4\pi\chi_{\text{c.g.s.}}$$

This point is of importance when the effect of magnetic anisotropy on chemical shifts is discussed. Further, the literature contains values of $\chi_{\text{c.g.s.}}$ expressed in two ways — as $\text{cm}^3 \text{ molecule}^{-1}$ and as $\text{cm}^3 \text{ mole}^{-1}$, differing by Avogadro's Constant.

- (iii) One item of uniformity in the present volume is that the recommended symbol B is used for magnetic induction field rather than the symbol H , which should be reserved for magnetic field intensity. The distinction is of little significance in c.g.s. since B and H are then of the same dimensions and approximately equal. However, in SI the units of B and H differ by Ξ , the permeability of the medium, which is usually of the

order of $4\pi \times 10^{-7} \text{ V A}^{-1} \text{ s m}^{-1}$. Unfortunately, many n.m.r. spectroscopists still use the symbol H (and compound the confusion by quoting gauss units rather than oersteds).

- (iv) As with other areas of chemistry, energy and entropy units are of importance for n.m.r. (e.g. for measurements of barriers to rate processes using n.m.r. bandshapes). Standardization on the calorie or the joule is only made in this volume within individual chapters. It may be noted that

$$1 \text{ cal}_{\text{th}} \equiv 4.184 \text{ J}$$

- (v) There appears to be some controversy over the definition (and hence units) of the reduced coupling constant, K , in SI. The original definition by Pople and Santry¹ (which won acceptance over the proposals of Lynden-Bell and Sheppard²) was expressed by them in two ways, as in equations (1) and (2):

$$K_{AB} = (2\pi/\hbar\gamma_A\gamma_B) J_{AB} \quad (1)$$

$$E_{AB} = (K_{AB})_{\alpha\beta}\mu_{A\alpha}\mu_{B\beta} \quad (2)$$

where E_{AB} is the energy perturbation caused by the interaction of magnetic moments $\mu_{A\alpha}$ and $\mu_{B\beta}$ (summation over α and β subscripts is assumed, in the normal convention for tensors). The units are usually cm^{-3} in the c.g.s. system (the values are normally of the order of 10^{20} cm^{-3} . For SI, McGlashan³ (or rather Whiffen) has chosen to re-define K by:

$$K_{AB} = 8\pi^2 J_{AB}/\Xi_0\gamma_A\gamma_B\hbar \quad (3)$$

where Ξ_0 is the permeability constant ($4\pi \times 10^{-7} \text{ V A}^{-1} \text{ s m}^{-1}$). Such a re-definition leaves K with the same units as reciprocal volume, as before. Earlier, however, Lynden-Bell and Harris⁴ suggested the retention of the definitions (1) and (2) in SI, and quoted a number of reduced coupling constants on this basis. They then have units* of $\text{N A}^{-2} \text{ m}^{-3}$ ($\equiv \text{kg m}^{-2} \text{ s}^{-2} \text{ A}^{-2}$). The relationship between the c.g.s. and SI units becomes:

$$1 \text{ N A}^{-2} \text{ m}^{-3} \equiv 10 \text{ cm}^{-3}$$

This latter method has the advantage that the definition (1) is a relationship in simple physical terms, and does not have the constant $\Xi_0/4\pi$ explicitly written (this constant will then only appear when expressions for K are derived in terms of VB or MO theory). The change of units may be felt to be a disadvantage, but it should be noted that a similar situation obtains for polarizability: in SI the equations have been retained and the 'dimensions' of the units therefore differ from those in the c.g.s. (e.s.u.) system. In Chapter 2 of this volume, Grinter has adhered to the choice of Lynden-Bell and Harris.

* The first printing of this book erroneously mentions the units as $\text{N A}^2 \text{ m}^{-3}$.

¹ J.A. Pople and D.P. Santry, *Mol.Phys.*, 1964, **8**, 1.

² R.M. Lynden-Bell and N. Sheppard, *Proc.Roy.Soc.*, 1962, **A269**, 385.

³ M.L. McGlashan, 'Physico-Chemical Quantities and Units', Royal Institute of Chemistry, 1971, (second Edition).

⁴ R.M. Lynden-Bell and R.K. Harris, 'Nuclear Magnetic Resonance Spectroscopy', Nelson, 1969.