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8

# 界面科学导论

G. T. 巴恩斯，I. R. 金特尔

原著第2版

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北京

图字：01-2012-2026



**图书在版编目(CIP)数据**

界面科学导论＝Interfacial Science: an Introduction，原著第2版：英文/(澳)巴恩斯(Barnes，G. T.)等编著．—影印本．—北京：科学出版社，2012
国外化学经典教材系列 8
ISBN 978-7-03-034146-4

Ⅰ.①界… Ⅱ.①巴… Ⅲ.①界面-理论-高等学校-教材-英文
Ⅳ.①O357.4

中国版本图书馆CIP数据核字（2012）第080729号

责任编辑：周 强／责任印制：钱玉芬／封面设计：耕者设计室

科学出版社 出版
北京东黄城根北街16号
邮政编码：100717
http://www.sciencep.com
新科印刷有限公司 印刷
科学出版社发行 各地新华书店经销
*
2012年5月第 一 版 开本：787×1092 1/16
2012年5月第一次印刷 印张：21 1/2
字数：433 000

**定价：78.00元**

（如有印装质量问题，我社负责调换）

# 第 1 版前言

尽管对于界面的研究已经经历了一个多世纪，但是它与其他学科的关联性只增不减，这归因于我们如今广泛地称之为纳米科学领域的迅速兴起。考虑到基本的功能和结构单元变得越来越小并且达到了分子尺度，界面的影响便无法忽略。

这就是化学、工程和材料科学等专业学生需要理解界面科学的重要性所在。尽管大部分物理化学的教科书都会包含界面或者表面这一章，但无非是提醒学生注意它们的存在，列出的提纲也十分简要。

当然，也有专门撰写界面和表面科学的教科书。其中涉及的一些实质性、权威性的内容，在本书中也有所体现。对于这样一个试图覆盖整个学科的教材，我们自然不能保证学科领域所有的内容在本书中均有所涉猎，因为我们发现其中既有较难的内容，也有类似数值计算的简单内容，两者之间的界线不能很好地协调。当我们想要把界面这门学科介绍给读者的时候，界线随即浮现，而打破这一界线便成为了我们主要的写作动力。

这本书是主要针对中高年级的化学及相关学科的本科生，同时可作为该领域及相关领域的研究生的入门介绍。我们假定读者已经掌握了一些物理化学的知识，尤其是热力学的知识，当然即便是没有这些背景知识，本书也可以很好地读懂。因为更加复杂的衍生问题已经被作者隐藏了，那些艰深的内容即便被略过也不会影响整本书的逻辑脉络。对于导师和更高层次的学生，我们提供了拓展阅读的参考文献，但是并没有穷尽所有的原始文献。

在撰写引言的时候，我们尽力呈现整个领域的概观，使得读者能够从定性和定量的角度对书中的内容全面把握。21 世纪已经被完全理解的基础科学知识是我们书中强调的重点。最新的研究结果在书中也有涉猎，但只包括了那些对于基本概念产生影响或者为表面科学带来其他特别兴趣的内容。固-固界面在大部分的电子器件中是一个基本的特征，因此成为了许多研究的课题并取得了一定的发展。这部分研究，我们很难在本书的一个短小的章节中讲述完全，因此固-固界面在本书中并没有涉及。

我们非常感谢之前和现在的同事以及学生们对这本书的编写所作出的贡献，为图形、表格、图片等提供的数据。他们是 Geoff Ashewell，Bronwyn Battersby，Ian Costin，David Gorwyn，Rob Lamb，Gwen Lawrie，Marylyn McGregor，Jian-Bang Peng，Jeremy Ruggles，Brendan Sinnamon，Roland Steitz，and Barry Wood.

我们还要感谢 Bob Hunter 百忙之中阅读了书稿的部分内容，并且提出了详细的意见，这些建议对本书的撰写极其有帮助。最终，我们把最特别的感谢给予我们的妻子 Beth 和 Jillian，感谢她们的容忍、耐心和理解。

# 第 2 版前言[①]

在第 2 版书稿中，我们除了更正第 1 版的一些错误外，还对语言进行了润色，填补了内容上的空白，并且加入了许多更为实质性的部分。此外，新增内容还包括由化学吸附衍生出来的讨论、多相催化、黏土矿物和一些生物界面领域新的以及衍生出来的话题。

我们还在书中介绍了实际工作中的例子，计算题的答案都放在每个问题结尾的方括号中。之所以选择这些实例，是因为它们或者强调了书中的某一方面，或者通过引入计算让读者对于相应的内容产生更深刻的认知。因此，读者应当将这些实例作为重要的部分来阅读。

George Blazak 提供了部分实例的数据，对于新材料有用的评论来自于 John Cotton 和 Bronwyn Battersby。

这一版书稿的筹备充分借鉴了读者对于第 1 版的反馈意见，并且得到牛津大学出版社(OUP)委托的匿名评论的帮助。我们同时诚挚感谢在书稿筹备过程中，牛津大学出版社的工作人员所给予的关注和鼓励。当然，还有我们的妻子们一贯的耐心和理解。

Geoff Barnes
Ian Gentle
Brisbane, 2010

① 本书前言、目录由北京大学化学与分子工程学院裴坚翻译。

# Acknowledgements

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# Units, symbols, and abbreviations

As in any field, there are certain accepted conventions used in symbols and abbreviations, and in this book we have tried to use accepted terminology where possible. Generally, the SI system of units and recommended symbols has been used; however, there are a few cases where additional symbols are needed or where some small modification to the recommendation is desirable.

## Units

There are significant advantages in working exclusively in SI units. These units consist of base units and derived units and are modified by prefixes (see Harrison & Ellis, 1984). Worked examples will be found throughout this book.

### Base and supplementary units

| | | |
|---|---|---|
| metre | m | unit of length |
| kilogram | kg | unit of weight (note that this is the base unit despite the 'k' prefix) |
| second | s | unit of time |
| ampere | A | unit of electric current |
| kelvin | K | unit of temperature |
| mole | mol | unit of amount of substance |
| candela | cd | unit of luminous intensity |
| radian | rad | supplementary unit of angle |
| steradian | sr | supplementary unit of solid angle |

### Derived units

Useful units with special names are listed below together with their equivalents in base units. Note the spaces between units.

| | | |
|---|---|---|
| hertz | $Hz = s^{-1}$ | unit of frequency |
| newton | $N = kg\ m\ s^{-2}$ | unit of force |
| joule | $J = kg\ m^2\ s^{-2}$ | unit of energy |
| watt | $W = kg\ m^2\ s^{-3}$ | unit of power |
| pascal | $Pa = kg\ m^{-1}\ s^{-2}$ | unit of pressure |
| coulomb | $C = A\ s$ | unit of electric charge |
| volt | $V = kg\ m^2\ s^{-3}\ A^{-1}$ | unit of electric potential difference |
| ohm | $\Omega = kg\ m^2\ s^{-3}\ A^{-2}$ | unit of electric resistance |
| siemens | $S = \Omega^{-1} = kg^{-1}\ m^{-2}\ s^3\ A^2$ | unit of electric conductance |
| farad | $F = A^2\ s^4\ kg^{-1}\ m^{-2}$ | unit of electric capacitance |

### Non-SI units

| | | |
|---|---|---|
| ångstrom | $Å = 10^{-10}$ m | unit of length |
| atmosphere | atm = 101325 Pa | unit of pressure |

| | | |
|---|---|---|
| electron volt | eV =* $1.602\times10^{-19}$ J | unit of energy (*equivalence not equality) |
| molar | M = mol $dm^{-3}$ | unit of concentration |

**Prefixes**

Those prefixes likely to be encountered in this book are given below. It is recommended that when inserting numerical values into an equation the prefixes be replaced by their numerical equivalents (with the exception of the k in kg). If this is done the answer will automatically be in the correct SI units with a power of 10 that can then be converted to the appropriate prefix. If the physical quantity is taken to a power, the prefix is also taken to that power. For example:

$$1\ \text{nm}^2 = 1\times(10^{-9}\ \text{m})^2 = 1\times(10^{-9})^2\ \text{m}^2 = 1\times10^{-18}\ \text{m}^2$$

Relevant prefixes are:

| | | | | | |
|---|---|---|---|---|---|
| tera | T | $10^{12}$ | centi | c | $10^{-2}$ |
| giga | G | $10^{9}$ | milli | m | $10^{-3}$ |
| mega | M | $10^{6}$ | micro | μ | $10^{-6}$ |
| kilo | k | $10^{3}$ | nano | n | $10^{-9}$ |
| deci | d | $10^{-1}$ | pico | p | $10^{-12}$ |

**Relationship between physical quantities and their units.**

The SI recommends that the following relationship be used:

physical quantity = numerical value × unit.

Thus, in labelling columns in tables or axes on graphs the appropriate label should have the form: *physical quantity*/unit, which means that only the numerical values should be shown in the column or along the axis. Examples will be seen throughout this book.

As well, the SI suggests that when numerical values are inserted into equations the units should also be inserted. Again, examples are given later.

## Symbols

Note that in the SI, symbols for physical quantities are printed in *italics*, whereas symbols for units are printed upright. Note that we will also print labels (such as substance M or phase β) upright. The symbols used are listed below:

| | |
|---|---|
| $A$ | total area of surface |
| $\hat{A}_{\mathrm{M}}$ | area per molecule of substance M |
| $a_i$ | activity of substance $i$ |
| $c_i$ | concentration of substance $i$ |
| $D$ | diffusion coefficient |
| $d$ | diameter of particle |
| $e$ | elementary charge |
| $E_{\mathrm{k}}$ | kinetic energy |
| $E_{\mathrm{b}}$ | binding energy |
| $F$ | force |

| | |
|---|---|
| $G$ | Gibbs free energy |
| $g$ | acceleration due to gravity |
| $H$ | enthalpy |
| $I$ | ionic strength (Eqn 9.17) |
| $M$ | molar mass |
| $m_i$ | mass of substance *i* |
| $N_A$ | Avogadro constant[1] |
| $N_i$ | number of molecules of substance *i* |
| $N_p$ | number of particles |
| $n$ | refractive index |
| $n_i$ | amount (in moles) of substance *i* |
| $n_i^\sigma$ | total adsorbed amount (in moles) of substance *i* |
| $P$ | pressure |
| $p$ | partial pressure or vapour pressure |
| $q$ | heat energy |
| $R$ | gas constant |
| $r$ | radius; transport resistance |
| $S$ | entropy; spreading coefficient |
| $T$ | temperature |
| $t$ | time |
| $U$ | internal energy |
| $V$ | volume |
| $\bar{V}$ | partial molar volume |
| $V_a$, $V_r$ | potential energy of attraction, repulsion |
| $u$ | velocity |
| $v$ | rate |
| $w$ | work energy |
| $x_i$ | mole fraction of substance *i* |
| $x$ | distance in the surface plane |
| $y$ | distance in the surface plane |
| $z$ | distance normal to the surface plane |
| $z_i$ | charge number of substance *i* |
| $\Gamma_i$ | adsorbed amount of substance *i* on unit area of surface |
| $\gamma$ | surface tension; shear strain |
| $\varepsilon$ | permittivity |
| $\varepsilon_0$ | permittivity of vacuum |
| $\varepsilon_r = \varepsilon/\varepsilon_0$ | relative permittivity (dielectric constant) |
| $\zeta$ | zeta (electrophoretic) potential |
| $\eta$ | viscosity |
| $\theta$ | fraction of surface covered by adsorbed film; contact angle; scattering angle |
| $\mu_i$ | chemical potential of substance *i* |
| $\Pi$ | surface pressure |
| $\Pi^{eq}$ | equilibrium spreading pressure |

[1] The unit of the Avogadro constant is usually given as $mol^{-1}$. However, in this book the constant is mostly used as a factor converting moles to molecules and thus the appropriate units are molecule $mol^{-1}$.

| | |
|---|---|
| $\Pi^{os}$ | osmotic pressure |
| $\pi$ | ratio of circle circumference to diameter = 3.1416 (to four places) |
| $\rho$ | density |
| $\phi$ | phase angle |

**Superscripts and subscripts**

| | |
|---|---|
| • | indicates a pure substance |
| $\alpha$, $\beta$ | indicate a bulk phase |
| S, L, G | indicate solid, liquid, or gas phase |
| $\sigma$ | indicates a surface excess quantity |
| $\ominus$ | indicates a standard state |

## Abbreviations

| | |
|---|---|
| AFM | atomic force microscopy |
| BAM | Brewster angle microscopy |
| BET | Brunauer, Emmett, and Teller (equation for gas adsorption) |
| CCD | charge-coupled device |
| cmc | critical micelle concentration |
| $C_{16}$TAB | cetyl trimethyl ammonium bromide |
| $C_n$OH | alcohol with *n* carbon atoms in chain |
| FTIR | Fourier transform infrared (spectroscopy) |
| GIXD | grazing incidence X-ray diffraction |
| LB | Langmuir–Blodgett (technique for depositing films on solids) |
| PEO | poly(ethylene oxide) |
| QCM | quartz-crystal microbalance |
| SAM | self-assembled monolayer |

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# 目　　录