化学反应体系的
线性特征

化学反应体系的线性特征和实用热力学分析

——一个原创性的化学研究方法

殷福珊 著

理想气体吉布斯
自由能估算方法

反应体系
实用热力学分析

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Some Linear Characters of
Chemical Reaction System
and Applied Thermodynamic Analysis
——A Creative Research Method for Chemistry

应用例——甲烷的
氨氧化反应制备甲胺

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摘要

本书包括两部分内容。化学反应体系的线性特征是一个新概念。它是用线性代数方法对发生化学反应时必须遵守的原子守恒定律的定性和定量描述。其中的计量限制矩阵也是首次被提出，它不仅是反应体系物料衡算和化学平衡分析的有力工具，更有助于判别并解决附加限制的有关问题。

热力学部分则介绍了适用于理想气体条件的几个实用的吉布斯自由能计算方法，以帮助判别一定反应条件下，各化学反应的热力学可行性。

上述两部分知识的组合，便可使读者能够自主地从事原创性的化学研究。

前言

本书是关于这一命题的第一部专著，包括两部分内容：化学反应体系的线性特征和化学热力学，重点在第一部分。本书的目的是向读者介绍一种如何开展化学化工领域的原创性研究。

化学反应体系的线性特征，是从数学方面对化学反应体系的定性和定量描述。只要给定一个反应体系中有哪些组分（包括原料、产物、副产物等），便可以建立起该体系的原子矩阵 $\overline{B}$。采用一种简便的矩阵运算方法，即可由 $\overline{B}$ 变换出计量系数矩阵 $\overline{A}$。$\overline{A}$ 包含了反应体系中组分间所有可能的简单计算系数方程式。从化学的角度，它们亦即所有可能的化学方程式，是我们建立该体系反应图式的基础。再通过同样的矩阵运算，可以由矩阵 $\overline{A}$ 变换出计量限制矩阵 $\overline{L}$。计量限制矩阵是作者提出的一个新概念，它不仅揭示了发生化学反应时各组分间必须遵循的定量关系，更重要的是依靠它理清了计量限制条件和附加限制条件的区别。利用上述概念和方法，我们能够摒弃一百多年来沿用的独立反应、关键反应以及独立反应的反应度等模糊概念。

附加限制问题，是建立反应图式时遇到的难题，也是以往学者们争论的焦点。本书中，首次提出了区别计量限制条件和附加

限制条件的方法。 又通过矩阵变换得到经修饰的计量系数矩阵 $\overline{A}_{\mathrm{m}}$ 和计量限制矩阵 $\overline{L}_{\mathrm{m}}$。 它们和原子矩阵 $\overline{B}$ 一起构成有附加限制条件时反应体系的线性特征。

基于上述分析，一百多年前由 Gibbs 提出的计量系数规则：

$$I \leqslant m - R_{\mathrm{B}}$$

被修正成等式 $\quad I = m - R_{\mathrm{B}} - k_1$

这里 k_1 是反应体系中线性独立附加限制条件数。

上述反应体系的线性特征，仅解决了数学问题。 计量系数方程不能揭示化学反应的方向性，也不一定能表示实际的化学反应过程。 因此，还必须结合具体的反应条件，对矩阵 $\overline{A}$ 或 $\overline{A}_{\mathrm{m}}$ 中每个计量系数方程式进行热力学运算，分析在一定的反应条件（包括温度、压力、进料条件等）下它所代表的化学反应能否进行、正向或反向、可逆或不可逆等。 相关的热力学计算主要聚焦于计算各计量系数方程式代表的化学反应的吉布斯自由能 ΔG，以及标准吉布斯自由能 ΔG^0。 这些是化学热力学中成熟的内容，已经积累了大量文献资料，包括针对各种实际反应体系提出的许多计算方法。 本书中我们仅选择接近理想气体状态的反应体系，介绍几种实用的计算 ΔG^0 的方法，用于估计相关的化学反应的热力学可能性。

具备了上述反应体系有关的数学知识和热力学知识，我们就可以独立自主地进行化学研究。 确定原料、目的产物以及可能的

中间产物和副产物后，先建立原子矩阵 $\overline{B}$；接着衍生出计量系数矩阵 $\overline{A}$ 和计量限制矩阵 $\overline{L}$；对每一个计量系数方程求出设定反应条件下的吉布斯自由能 ΔG，在此基础上判断哪些化学反应有最大的热力学可能性，进而指导动力学实验研究。这样，我们就可以摒弃长期沿用的从查文献、找专利出发模仿前人的研究方法，走出自主创新的路来。

本书中应用的矩阵变换方法，得益于笔者三十多年前在美国哥伦比亚大学师从 John Happel 教授时获得的知识。当时，我们经常讨论反应图式问题，各持己见。因为理由不充分，谁也说服不了谁。后来 Happel 教授和一位数学家一起发表了用矩阵变换方法分析催化反应机理的文章。笔者回国后深入研究该方法，于 1986 年取得突破，使得这种矩阵变换方法成为分析复杂反应体系的有效工具。1992 年，附加限制这一难题得到解决，方法臻于成熟。

本书的目的，是为化学化工研究工作者提供一个能够独立自主进行创新研究的方法。读者对象是大学本科以上，已经具备了线性代数和化学热力学基本知识的专业技术人员。为此，本书内容叙述尽量深入浅出，便于理解和应用。书中列举了一些例题，对于理解和应用本方法是有教益的。有趣的是，反应体系的数学分析，是全部基于同一类型的矩阵初等变换完成的，证明这种方法具有显著优点。在计算机技术飞速发展的今天，倘若能够完成相应的计算机编程，必将大大减轻计算工作的强度，从而使更多读者能够掌握并运用此方法。遗憾的是本人年事已高，这项工作只能留待后人来做。

为什么事隔二十多年后重新捡起这项工作？ 简而言之，人在江湖身不由己。 这过去的二十年，笔者主要从事表面活性剂和油脂化工领域的研发工作，并在现代工业生物技术这一新兴领域投入了相当多的时间和精力。 近年，在浙江赞宇集团研发中心和无锡华格新材料有限公司同仁们的协助下，本书的电子版才得以完成。 笔者的学生郭春伟博士帮助做了许多电脑应用方面的工作。另外，江南大学化学和材料工程学院给予本工作全力支持并承担了本书的大部分出版费用，中国洗涤用品工业协会同样给予了财政资助。 本人在此一并表示深深的谢意！

但愿此书对化学化工界基础性研究，对我国学术界的创新研究，对青年化学工作者的成长能够起到一定的帮助作用。

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Preface

It is the first book on this title. It consists of two sections: some linear characters in chemical reaction system and its thermodynamic analysis. The key point is the first part. The purpose of this book is to introduce a creative method of chemical research for readers.

The linear character of chemical reaction system is both a qualitative and quantitative mathematical descriptions on a reaction system. As long as all components in a chemical reaction system are given or known, we can set up its atomic matrix $\overline{B}$ immediately. Here the terminology "components" means all compounds including raw materials, intermediates, products and by-products involved in chemical reactions. By a simple matrix transformation, the stoichiometric coefficient matrix, $\overline{A}$, could be obtained from matrix $\overline{B}$. Matrix $\overline{A}$ contains all possible stoichiometric coefficient equations of given reaction system. From a view of point of chemistry, matrix $\overline{A}$ is a collection of all possible chemical reaction equations. So, matrix $\overline{A}$ provides a base for establishing a reactive scheme for given system. By similar matrix transformation, a stoichiometric restrictive matrix, $\overline{L}$, could be derived from matrix $\overline{A}$. Here matrix $\overline{L}$ is a

new concept. Matrix $\overline{L}$ is not only useful in description of the quantitative variation of components during chemical reaction, but also is a powerful tool to distinguish the difference between stoichiometric restriction and additional restriction. Based on above concepts and methods, we are able to withdrew some unclear concepts such as independent reaction, key reaction, and independent reaction degree etc. which has been traditionally used for more than one hundred years in chemistry.

Additional restriction is a main problem for establishing correct reaction scheme and also the main arguments among many scholars. In this book, for the first time a method was set up to distinguish the stoichiometric restriction and additional restriction, and again by matrix transformations we derive both modified stoichiometric coefficient matrix, $\overline{A}_m$, and modified stoichiometric restrictive matrix, $\overline{L}_m$. Matrix $\overline{A}_m$ and $\overline{L}_m$, together with atomic matrix $\overline{B}$, form the basic linear characters of a reaction system with additional restriction.

Based on the knowledge of above matrix transformations, the Gibbs's stoichiometric rule which was established one hundred years ago:

$$I \leqslant m - R_B$$

could be modified as:

$$I = m - R_B - k_1$$

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here k_1 is the number of independent linear additional restriction of reaction system.

However, above linear characters is only a mathematical description of a chemical reaction system. Stoichiometric coefficient equations can not predict the direction of possible chemical reactions. Therefore, we need the thermodynamic knowledge to predict the possibility of every chemical reaction in matrix $\overline{A}$ or $\overline{A}_m$. Under given reactive conditions such as temperature, pressure, feeding raw materials etc., thermodynamic calculation will tell us about the possibility, direction, and equilibrium yield etc., of every chemical reaction. For our purpose, we are mainly concerned about Gibbs free energy, ΔG and standard Gibbs free energy, ΔG^0 for every related chemical reaction in matrix $\overline{A}$. There are many methods on such calculations in books and literature. In this book we only introduce a few methods to deal with the reaction system under ideal gas state.

Based on the knowledge of matrix transformation and thermodynamic analysis, we'll be able to research chemical synthesis independently: according to given raw materials and purposed products, and proposed intermediates and byproducts, an atomic matrix $\overline{B}$ may be set up immediately. Then the stoichiometric coefficient matrix $\overline{A}$ and stoichiometric restrictive matrix $\overline{L}$ can be derived. Under given reactive conditions we may calculate the Gibbs free energy ΔG for every stoichiometric coefficient equation in matrix $\overline{A}$, then we may interpret which chemical reactions

have thermodynamic possibility. Changing supposed reactive conditions will get other possibilities. All these theoretical analysis make us a better understand on supposed reaction system and are useful for guiding kinetic research. In this way, we do not need to looking for literature or patent firstly and to working following. Instead, we can start to investigate a chemical reaction system independently.

Author got knowledge of this kind of matrix transformation thirty years ago when I was in Columbia University, New York, USA, as a visiting scholar. I spent almost three years working with Dr. John Happel and established excellent relationship with him. After I came back to China I continued the research on this subject and got breakthrough in 1986. In 1992 the problem on additional restriction was solved and a few papers were published.

The purpose of this publication is to provide an independent creative method for chemistry research. Readers of this book should have fundamental knowledge on linear algebra and thermodynamics. For easy understand and application, a couple of examples were included in text. The interesting thing is the mathematical analysis of reaction system is all based on the same elemental matrix transformation indicating the great advantage of the method. Today computer technology has had great progress. If the matrix operation could be programmed, it will be very helpful to simplify matrix calculations so that more readers could apply this method with easy. Unfortunately, to my age such work is beyond my

scope.

I appreciated my friends from Zhejiang Zanyu Group, Hangzhou, for their assistant for electronic edition of this book. Also, my student Dr. Chunwei Guo spent a lot of time on PC for book. Last but not least, my sincere thank to the School of Chemical and Material Engineering, Jiangnan University, for their financial support for publication, as well as partly from China Cleaning Industry Association.

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