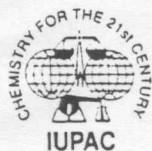


Chemical Thermodynamics

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INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY



Chemical Thermodynamics

A 'Chemistry for the 21st Century' monograph

EDITED BY

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Foreword

The International Union of Pure and Applied Chemistry (IUPAC) conceived the series 'Chemistry in the 21st Century' to bring to the attention of a wide audience the role that chemistry will play in the future development of society and the preservation of our environment. This imaginative series has therefore set out to produce volumes which contain essays on topics within chemistry written by experts, with the non-expert but interested individual as the largest readership. The interested individuals may comprise those who wish to study chemistry, make use of it or enter research in the subject.

Within the IUPAC Commission 1.2 on Chemical Thermodynamics, the initiative of the Union was accepted with enthusiasm. Thermodynamics has formed one of the foundations of much of chemistry, in teaching, research and application, for almost 150 years. For that very reason, it is often thought of as a subject that is worthy, although no longer fashionable, and that has little relevance to the future development of chemistry. That image of worthiness and importance has been enhanced by the work of the Commission itself after early years in the standardization, codification and presentation of thermodynamics and the thermodynamic properties of materials. In particular, the series 'International Thermodynamic Tables of the Fluid State' has now reached its thirteenth volume and provides for users worldwide the properties of single fluids that are agreed to be the basis of international agreements for both science and trade.

The present volume should change that perception dramatically. Professor Trevor Letcher, the editor, has, with characteristic boundless energy, brought together 45 authors to contribute to 27 topics within the field of thermodynamics. The topics cover the entire range of chemistry and vary from the most fundamental to industrial applications. As such, they represent a summary of the fields to which the Commission on Chemical Thermodynamics of IUPAC has been dedicated since its inception over 20 years ago. The authorship also spans the globe (authors come from 12 countries) and vividly illustrates the benefits which IUPAC has brought and continues to bring to chemistry through its internationalization of the subject.

It is my pleasure, as Chairman of Commission 1.2 of IUPAC at the inception of the project, to thank Professor Letcher especially, as well as his team of authors, for making the idea become a reality and to commend the book to readers.

W.A. Wakeham

Preface

Chemical thermodynamics is a fundamental part of chemistry and is included in any curriculum designed to educate an all-round chemist. However, unlike most areas of chemistry, its fundamentals are firmly rooted in the 19th century. This has sometimes created the image that chemical thermodynamics is important only from a historical point of view. We hope that this collection of essays will serve to counteract such an impression. It introduces the reader to 27 topics in chemical thermodynamics, each of which illustrates a new and potentially useful area of study. The classical areas of chemical thermodynamics involving the measurement of bond enthalpies, properties of gas mixtures and liquid mixtures, standard Gibbs energies and enthalpies of formation, etc. are not included here, as they have been exhaustively reviewed and discussed elsewhere.

The aim of this collection is to show that the applications of chemical thermodynamics are many and are related to the very latest developments in chemistry. Chemical thermodynamics is alive and well and is not only making a valuable contribution to our understanding of the world about us, but is helping to create a better world. This is particularly important as we stand on the brink of an unprecedented increase in world population and pollution and the possibility of a significant climatic change. Each essay is aimed not only at those working in the area, but also at the general chemist, at the prospective researcher and also at those involved in funding chemical research.

The areas covered include:

- separation technology, including membrane techniques, solvent extraction and supercritical properties;
- colloids and microemulsions;
- electrolytes;
- adsorption;
- nuclear applications;
- theoretical and quantum chemistry;
- polymer science;
- microgravity;
- new materials including amorphous materials and glasses;
- enzyme-catalysed reactions;
- biology and cell biology;
- medicine and pharmacy;
- food science;
- petroleum chemistry.

This collection owes its origins to the involvement of all the members of the IUPAC Commission 1.2, who debated its existence, plotted its direction and agreed on its format, through meetings, e-mail messages and discussions during 1996 and 1997. Special tribute must go to our Chairman, Professor Bill Wakeham of Imperial College London, and also to good friends and ex-members of our Commission, Dr Gerd M. Olofsson of Lund University, Professor Gus Somsen of Vrije Universiteit, Amsterdam, and Dr Pat A.G. O'Hare of NIST, Gaithersburg, for their support and encouragement.

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1 The Basis for the Synthesis, Design and Optimization of Thermal Separation Processes

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1 Introduction

Separation processes are of great importance not only in the chemical and petrochemical industry but also in refineries, gas processing industry, biotechnology, etc. As shown in Fig. 1.1, a chemical process can be roughly divided into three steps: pre-treatment, reaction and separation. Even though the reactor can be considered as the heart of a chemical plant, the greatest part of the costs (investments, operating costs) are borne by the separation step, in which the compounds leaving the reactor (usually a multicomponent system) are separated in such a way that the desired products are obtained with the desired purity, side-products are removed and unconverted reactants recycled. The synthesis, design and optimization of chemical processes are performed today by solving the mass and energy balance of the mathematical model for the partial or complete plant with the help of process simulators. In the case of separation processes, either the equilibrium stage concept or a rate-based approach is used. In both cases, the pure component and mixture properties (phase equilibria, enthalpies, etc.) utilized for the simulation are of decisive importance in respect of the simulation results. For the development and optimization of separation processes in particular, a reliable knowledge of the phase equilibrium behaviour of the system to be separated is required.

Different thermal separation processes can be applied for the separation of the mixture leaving the reactor. The basic principle of a thermal separation process is shown in Fig. 1.2. With the help of a separating agent (energy, mass separating agent), the system to be separated is divided into two streams of different composition. When enough stages are realized, the compounds can be obtained with the desired purity. Depending on the type of separating agent, different separation processes can be distinguished.

The most important large-scale separation processes are listed in Table 1.1. In the case of distillation (crystallization), energy is used as the separating agent and the composition difference between the liquid and the vapour (solid) phase is utilized for the separation. In other separation processes (extraction, absorption, adsorption, membrane processes), a mass separating agent, such as a selective solvent, adsorbent or membrane, is applied, instead of energy, to obtain the 'second stream'.

When separation problems occur (azeotropic points, eutectic behaviour, etc.), hybrid processes can also be applied, for example the combination of distillation with crystallization, adsorption or membrane processes. With the help of suitable solvents also, the disadvantage of crystallization processes (only one product) can be eliminated (extractive or adductive crystallization). In a chiral environment, even racemates can be successfully separated.

Of particular interest for reversible or consecutive reactions are reactive separation

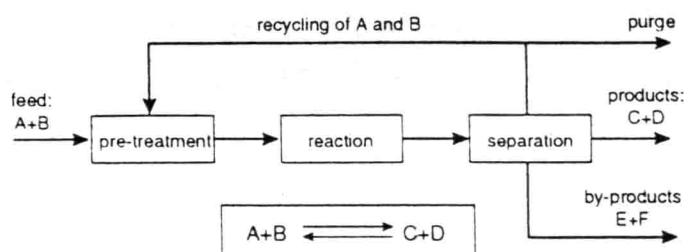


Figure 1.1. Basic structure of a chemical plant.

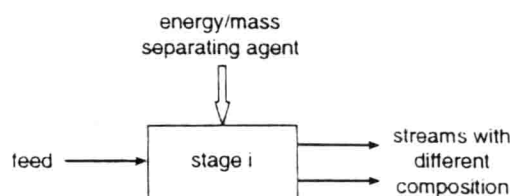


Figure 1.2. Basic principle of a thermal separation process.

Table 1.1. Overview of industrial separation processes.

Mixture	Separating agent	Separation process
Liquid	Energy	Distillation
	Energy + suitable solvent	Azeotropic and extractive distillation
	Selective solvent	Extraction
	Supercritical fluid	Supercritical fluid extraction
	Energy	Crystallization
	Adsorbents	Adsorption
	Membrane	Membrane process
Gas	Selective solvent	Absorption
	Adsorbents	Adsorption
	Membrane	Membrane process
Solid	Selective solvent	Solid-liquid extraction
	Supercritical fluid	Supercritical fluid extraction

processes, such as reactive distillation, reactive extraction, membrane reactors, etc. In particular, these processes permit much higher conversions and selectivities, simplify further separation steps and reduce recycle streams.

Depending on the thermodynamic behaviour and the number of components leaving the reactor, the separation step can be quite complex. The number of possible separation sequences, S_n , increases dramatically with the increasing number of components, n , and separation processes, T , considered. For $T = 1$ (e.g. only distillation) and $T = 2$, the resulting number of possible sequences is given in Table 1.2 for different numbers of components. However, with the help of heuristic rules, this number can be reduced to the most economical ones.

When the different separation processes are compared, great advantages become apparent for distillation processes. One reason is that the energy used as separating agent can easily be removed at the top of the column. In the case of mass separating agents, a regen-

Table 1.2. Number of possible sequences for different numbers of components.

	Number of components, n		
	4	6	10
Number of sequences for $T = 1$	5	42	4862
Number of sequences for $T = 2$	40	1344	2 489 344

eration (e.g. of the solvents or adsorption medium) is required. In the case of membrane processes, mechanical stability and fouling can cause problems. Furthermore, distillation allows a simple realization of a large number of stages, since, because of the large density difference, the coexisting liquid (L) and vapour phase (V) can, in contrast to extraction (two liquid phases) or crystallization processes (crystals, mother liquor), be easily separated and also the transport of the two fluid phases causes no problem. The latter two advantages are the main reasons why, even for the separation of azeotropic systems distillation processes, such as pressure swing, azeotropic and extractive distillation processes are applied. In the latter cases, energy as well as a suitable solvent is also used to realize the separation. The above-mentioned advantages are the main reasons for the application of distillation processes to 90% of the separation processes in the chemical industry. When the chemical and petrochemical industry, as well as refineries and the gas processing industry, are considered, the yearly throughput of distillation columns is about 5.2×10^9 t/year [1]. The main disadvantage is that distillation processes exhibit a high energy consumption. Thus, in 1989 in the USA, around 3% of the total energy consumption was required to run about 40 000 distillation columns [2].

The proper realization of the separation step is complex. Apart from the question of how to arrange the sequence, separation problems (azeotropic points, etc.) have often to be considered. It is the objective of process development to find the most economical solution for the given separation problem. During the development of the separation process, the chemical engineer has to decide, for example:

- whether an alternative separation process e.g. extraction, crystallization, absorption, adsorption, membrane process, supercritical extraction, can compete with the baseline process (distillation);
- whether separation problems have to be taken into account (azeotropic points, poor separation factors);
- how to solve special separation problems (special distillation process, hybrid process, etc.);
- which selective solvent or solvent mixture should be applied, e.g. for azeotropic or extractive distillation, extraction, absorption, to obtain a high selectivity and capacity;
- what is the most economical separation sequence;
- how many stages (column height) are required for the given separation process.

All these tasks require a reliable knowledge of the phase equilibrium behaviour of the multicomponent system, including all subsystems, to be separated as a function of composition, temperature and pressure. For one stage, the problem is shown in Fig. 1.3. The typical question asked by the chemical engineer is: 'What is the pressure P and the composition in phase β , when phase β is in equilibrium with phase α at a given temperature T ?' Depending on the phases involved, one can distinguish between vapour-liquid (VLE), liquid-liquid

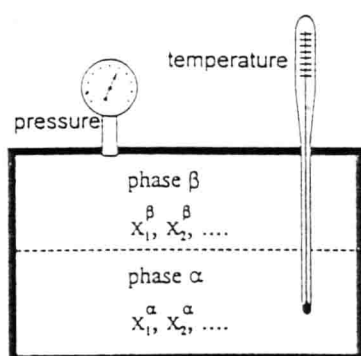


Figure 1.3. Equilibrium stage.

(LLE), solid–liquid equilibria (SLE), gas solubilities, etc. Sometimes more than two phases have to be taken into account, e.g. vapour–liquid–liquid equilibria (VLLE), as for the separation of *n*-butanol–water or ethanol dehydration processes.

Various reliable and partly computer-driven techniques have been developed for the measurement of the different phase equilibria. However, the measurement of phase equilibria for multicomponent systems is very time-consuming. For example, the measurement of a 10-component system at one temperature (pressure), including all binary (45 systems), ternary (120 systems) and higher systems would require about 37 years, when data in 10 mol% steps are measured [3]. This time factor illustrates the importance of thermodynamic models which allow the reliable prediction of the phase equilibrium behaviour for the system to be separated using only binary data. A large number of data for binary systems (>30 000 isotherms or isobars) have already been published and the measurement of all binary and pure component data for the 10-component system mentioned would only require around 42 days [3] instead of 37 years.

2 Phase equilibrium thermodynamics

Following Gibbs phase equilibrium rules, the chemical potentials μ_i of the different components show the same values in the existing phases $\alpha, \beta, \gamma, \dots$:

$$\mu_i^\alpha = \mu_i^\beta = \mu_i^\gamma = \dots \quad (1)$$

This equilibrium condition can be substituted at any time by the so-called isofugacity criterion introduced by Lewis:

$$f_i^\alpha = f_i^\beta = f_i^\gamma = \dots \quad (2)$$

However, neither of these relations is very helpful in practice. To obtain reliable relations between the measurable quantities, mole fraction (x_i (liquid phase), y_i (vapour phase)), pressure P and temperature T , auxiliary quantities such as activity coefficients γ_i and fugacity coefficients ϕ_i have been introduced to describe the fugacities f_i in the different phases. With the help of these auxiliary quantities, suitable relations can be derived to describe the different types of phase equilibria. For VLE, the following two different relations can be obtained, starting from the isofugacity criterion in equation (2):

Approach A: $x_i \phi_i^L = y_i \phi_i^V$ (3)

Approach B (simplified): $x_i \gamma_i P_i^s = y_i P$ (4)

Using these relations two different expressions for the distribution coefficients (K factors) K_i and the separation factors α_{ij} can be obtained. These quantities describe the enrichment of the component i and the separability of components i and j .

$$K_i = \frac{y_i}{x_i} = \frac{\phi_i^L}{\phi_i^V} = \frac{\gamma_i P_i^s}{P} \quad (5)$$

$$\alpha_{ij} = \frac{K_i}{K_j} = \frac{\phi_i^L \phi_j^V}{\phi_i^V \phi_j^L} = \frac{\gamma_i P_i^s}{\gamma_j P_j^s} \quad (6)$$

Starting from the isofugacity criterion, similar simple relations can also be derived for LLE, SLE, the solubilities of gases (solvents) in solvents (polymers), and so on.

The most important factor in obtaining reliable K and separation factors for multicomponent systems is a reliable description of the deviation from ideal behaviour in the different fluid phases as a function of composition, temperature and pressure. While in approach A the real behaviour in the liquid and vapour phase is described with the help of fugacity coefficients, ϕ_i , in approach B activity coefficients, γ_i , are used to account for the deviation from ideal behaviour in the liquid phase.

The required fugacity coefficients for the liquid and the vapour phase can be obtained by means of an equation of state (EOS) which is able to describe the pressure–volume–temperature (PVT) behaviour of both fluid phases. The first suitable equation to describe the PVT behaviour of the liquid and the vapour phase was the van der Waals EOS published in 1873. In the van der Waals EOS, a repulsive parameter b and an attractive parameter a are used to describe the PVT behaviour, including the two-phase region. This was the first equation which permitted a description of condensation, vaporization and critical phenomena using only two parameters, which can be obtained from critical data (e.g. critical pressure P_c and critical temperature T_c). To extend the applicability of EOS to mixtures, reliable mixing and combination rules for the two parameters are required.

In approach B, the vapour pressures, P_i^s , of the compounds as a function of temperature and a model for the activity coefficients are required to describe the activity coefficients as a function of composition and temperature (pressure). For the derivation of suitable expressions one can start from a model for the excess Gibbs energy, g^E , using the following relation [3]:

$$RT \ln \gamma_i = \bar{g}_i^E = \left(\frac{\partial g^E}{\partial n_i} \right)_{T, P, n_j \neq n_i} \quad (7)$$

$$g^E = RT \sum_i x_i \ln \gamma_i = \sum_i x_i g_i^{-E} \quad (8)$$

The observed temperature dependence of the activity coefficients can be described by means of the Gibbs–Helmholtz relation [3], using partial molar excess enthalpy data \bar{h}_i^E , which can readily be obtained, e.g. by using isothermal flow calorimetry:

$$\left(\frac{\partial \ln \gamma_i}{\partial 1/T} \right)_{P, x} = \frac{\bar{h}_i^E}{R} \quad (9)$$