Recent Work on Silicate and Related Systems Involving Chemical Components of Illinois Sedimentary Rocks*

F. V. Tooley

Illinois State Geological Survey, Urbana, Illinois

INTRODUCTION

The taking from the earth of various materials and the utilization of them, either directly or indirectly, in the production of socially useful objects, is as old as man himself. As milestones in this development might be mentioned the construction of caves and mud shelters for habitation. Later, with the discovery of fire, came the burning of crude clay wares both for structural and artistic purposes, and the production of crude glass. Out of these humble beginnings studies of the relationships between chemical composition of materials taken from the earth, temperature, and properties of the finished product have been slowly developing through their empirical stage and are in the present gaining a truly scientific foothold in the accumulated experience of civilization. Today we have better cements, glass, refractories, bricks, insulation materials, steel, and better building materials in general chiefly because we understand these relationships more thoroughly. In the present paper it is desired to present in necessarily brief form, considering the immensity of the subject, a glimpse of the state of high-temperature research on silicate and related systems.

The Basis of Recent Advances

Advances in high temperature silicate chemistry are the result of a combination of developments both on the theoretical and practical side. Of great significance on the theoretical side has been the phase rule of Willard Gibbs, the theorem of Le Chatelier and its quantitative expression in the form of the Clausius Clapeyron equation. Practically, recent advances in the fields of high temperature furnaces, thermoelectric pyrometry, microscopy, and the development of the quenching method and other techniques by the Geophysical Laboratory in Washington have been of major importance. The general impetus given work in the field of high temperature silicate chemistry by this latter institution both in the development of new techniques and apparatus, and in performing a tremendous amount of experimental research is deserving of the highest praise.

Experimentally, data for the construction of diagrams illustrating phase relationships at equilibrium are obtained by holding intimate mixtures, of definite composition, expressible in terms of the components of the system investigated, at a definite temperature, allowing the system to come to equilibrium and determining the relative amounts and the nature of the phases present under these conditions.

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The Body of Experimental Data

Upon examination of the average composition of the lithosphere[1] it is of little wonder that the greater part of researches on silicate and related systems have dealt with those systems the composition of which can be expressed by some combination of the oxides, SiO_2, Al_2O_3, CaO, MgO, FeO, Fe_2O_3, Na_2O and K_2O in varying proportions. On the calcined, or CO_2 and H_2O free basis, roughly 98 per cent of both igneous and sedimentary rocks is represented by these oxides. Consider further the position of these materials in industry. Ordinary portland cement, cements containing granulated blast furnace slag, pozzolanas and pozzolanic cement, and aluminous cement can all be represented in systems of components chosen chiefly from the above oxides. Likewise is this true of ordinary glass, silica, dolomite and fireclay refactories, bricks, tile, whiteware, porcelain, rock, slag and glass wool. Were we to imagine our present civilization minus cement, steel and glass, as we now know them, the importance of scientific information on systems composed of these oxides becomes strikingly apparent.

Although a detailed analysis of any of the individual systems studied cannot be given, the type of information procured in the field of research on silicate and related systems has to do, in the majority of cases, with the relationship of composition and temperature to the formation of compounds, eutectics, solid solutions, immiscible liquids, fields of stable phases, the distribution of phases, and to the physical properties of certain products derived from the systems. Tables I, II and III illustrate silicate and related systems on which work of this nature has in some degree been performed. One of the most pleasing phases of this work is the wide applicability of results to any problems involving the components of the particular system studied, i.e., its fundamental character. Thus the $CaO\text{-}Al_2O_3\text{-}SiO_2$ system has been helpful in problems not only in the cement industry, but in problems of the metallurgical and ceramic fields as well. Indeed, much of the work on phase equilibria performed by the Geophysical Laboratory in Washington, primarily concerned with geological application, has contributed equally as much in the industrial field.

This body of information is related fundamentally to the utilization of Illinois sedimentary rocks: In the first place the compositions of Illinois rocks can be expressed almost solely in terms of the oxides previously shown to be the major components in systems including the majority of products in the cement and ceramic industries, and the major components in metallurgical slags; as a matter of fact, a considerable Illinois production is utilized by these industries. Secondly, the complete phase equilibrium data of, and the properties of the various materials occurring within systems formed from the components in the sedimentary rocks are not fully known. These facts have been instrumental in developing the viewpoint on the part of the Illinois State Geological Survey that certain carefully selected avenues of research might contribute valuable information in the field of non-fuels technology in the State, both in the creation of new products and the improvement of old. The third point looks into the future a considerable distance, perhaps. A mixture of silicates in the molten state when allowed to cool delivers crystalline materials from solution, not haphazardly, but in an ordered manner predictable from phase equilibrium data. This suggests the possibility of extracting, by fractional crystallization from a cooling melt, pure minerals to be used, after cooling and grinding, as such, or in combination with other materials for the synthesis of new products. Likewise can be visualized a "silicate alloy" industry, preparing silicate glasses of desired composition and grain size to be utilized as the glassy bonding materials in ceramic wares.

Silicate Systems

Completely or partially studied by various investigators from a standpoint of phase equilibrium relationships and other properties. These studies were made at relatively high temperatures in all but a few cases.

TABLE I

- SiO_2
  - Binary
    - Al_2O_3
    - CaO
    - MgO
    - FeO
    - Fe_2O_3
    - Na_2O
    - $K_2O.SiO_2$
    - MnO
    - PbO
    - $CaO.SiO_2$
    - $Na_2O.SiO_2$
    - K_2CO_3
    - Na_3AlF_6
    - SrO
    - BaO
    - Li_2O
    - CaS
    - Pb_3O_4
    - ZnO
    - B_2O_3
    - SnO
    - ZrO_2
    - TiO_2
    - BeO
    - Cr_2O_3
    - MnS
    - MnO
  - Ternary
    - CaO | Al_2O_3, MgO, FeO, Fe_2O_3, Na_2O, K_2O, CaF_2, BaO, SrO, TiO_2, Li_2O, P_2O_5, CO_2, H_2O, MnO, B_2O_3
    - Al_2O_3 | MgO, FeO, Fe_2O_3, Na_2O, K_2O, Na_3AlF_6, TiO_2, Li_2O, MnO, BaO, ZnO, H_2O
    - Na_2O | Fe_2O_3, MgO, K_2SiO_3, $K_2Si_2O_5$, ZrO_2, B_2O_3, CO_2, H_2O, NaF
    - $Na_2O.SiO_2$ | $K_2O.SiO_2$, $CaO.SiO_2$, Fe_2O_3
    - K_2O | PbO, MgO, CO_2, H_2O
    - FeO | MgO, Fe_2O_3, SnO, MnO
    - Fe_2O_3 | ZnO
    - MnO | TiO_2
    - Pb_3O_4 | K_2CO_3
    - CuO | V_2O_5
    - Al | S
    - Fe | S
  - Quaternary
    - CaO | Al_2O_3—MgO, Al_2O_3—Fe_2O_3, Al_2O_3—Na_2O, B_2O_3—Na_2O, FeO—Fe_2O_3, MgO—FeO, TiO_2—MgO, TiO_2—MnO
    - Al_2O_3 | FeO—Fe_2O_3, K_2O—Na_2O, CaO—TiO_2, CaO—K_2O, Na_2O—FeO, K_2O—Fe_2O_3
    - Na_2O | BaO—CO_2

Systems of more than four components:

SiO_2—CaO—Al_2O_3—MgO—Na_2O
SiO_2—CaO—Al_2O_3—MgO—K_2O
SiO_2—CaO—Al_2O_3—MgO—Na_2O—Fe_2O_3—FeO
SiO_2—Si—MnO—Mn—FeO—Fe

TABLE II

Systems Without SiO_2

CaO	MgO Al_2O_3 Fe_2O_3 B_2O_3 ZrO_2
NaF	AlF_3 KF CaF_2 PbF_2 CdF_2
AlF_3	KF LiF
MgF_2	LiF CaF_2
KF	BaF_2
B_2O_3	Li_2O Na_2O CdO MnO PbO

Al_2O_3	MgO CaF_2 ZnO Cr_2O_3 TiO_2
ZrO_2	ThO_2
PbO	PbF_2 Bi_2O_3 As_2O_5 V_2O_5 MoO_3 CrO_3 WO_3
FeO	MgO Al_2O_3
Na_2O	TiO_2 As_2O_5 MoO_3 WO_3
K_2O	As_2O_5 MoO_3 WO_3
TiO_2	ThO_2

CaO	Al_2O_3—K_2O Al_2O_3—Na_2O Al_2O_3—MgO Al_2O_3—Fe_2O_3
NaF	CaF_2—AlF_3
MgO	FeO—Fe_2O_3
Fe_2O_3	Fe_3O_4—O_2
Na_2O	K_2O—B_2O_3 K_2O—As_2O_5 K_2O—CrO_3 K_2O—WO_3 K_2O—MoO_3 MoO_3—WO_3
PbO	CrO_3—SO_3 MoO_3—WO_3 MoO_3—Bi_2O_3 WO_3—Bi_2O_3 PbF_2—As_2O_5 PbF_2—V_2O_5
Al_2O_3	NaF—AlF_3 NaF—AlF_3—CaF_2

TABLE III

Melting Diagrams

MgO	NiO
	CoO
	Al_2O_3
	Cr_2O_3
	Fe_3O_4
	Mn_3O_4
	SiO_2
	TiO_2
	ZrO_2
	Cu_2O
	CaO
	BaO
	SrO
	BeO
	CeO_2
	La_2O_3
SiO_2	K_2O
	Rb_2O
	Cs_2O

Al_2O_3	CaO
	BaO
	SrO
	MgO
	NiO
	CoO
	TiO_2
	SiO_2
	BeO
	Cu_2O
	ZrO_2
	ThO_2
	CeO_2
	La_2O_3
	Mn_3O_4
	Fe_3O_4
	Ga_2O_3
	Cr_2O_3
CeO_2	CaO
	Cr_2O_3
	Fe_3O_4
	Mn_3O_4
	ZrO_2

ZrO_2	CaO
	SrO
	BaO
	BeO
	MgO
	ZnO
	NiO
	CoO
	Al_2O_3
	Cr_2O_3
	Fe_2O_3
	Mn_3O_4
	La_2O_3
CaO	Mn_3O_4
	Cu_2O
	TiO_2
	CoO
	NiO
	ThO_2
	Cr_2O_3

ZrO_2	CeO_2—Ce_2O_3
	BeO—CaO
	BeO—CeO_2
	ThO_2—CaO
	ThO_2—MgO
BeO	CaO
	CeO_2
	CoO
	Cr_2O_3
	Cu_2O
	Fe_3O_4
	La_2O_3
	Mn_3O_4
	NiO
	ThO_2
	TiO_2

Cone Deformation Diagrams

$Al_2O_3.2SiO_2$—CaO
$Al_2O_3.2SiO_2$—MgO
$Al_2O_3.2SiO_2$—FeO
$Al_2O_3.2SiO_2$—$K_2O.Al_2O_3.6SiO_2$
Microcline—steatite
Microcline—albite
Orthoclase—CaO
Orthoclase—MgO
Albite—CaO
Albite—MgO
Feldspar—Flint—Kaolin

BIBLIOGRAPHY

1. The Data of Geochemistry: F. W. Clarke U. S. Geological Survey Bulletin 770, p. 34.
2. A Compilation of Phase-Rule Diagrams of Interest to the Ceramist and Silicate Technologist: F. P. Hall and Herbert Insley. Journal of the American Ceramic Society *16,* 455-567 (1933).
3. *Supplement to* A Compilation of Phase-Rule Diagrams of Interest to the Ceramist and Silicate Technologist: F. P. Hall and Herbert Insley. Journal of the American Ceramic Society *21,* 113-157 (1938).

Note: Due to lack of space it is impossible to include in the bibliography references to all the systems in the Tables. Systems not referred to in reference 2 above will be gladly furnished by the author.

Since this paper was presented, a good deal of phase equilibrium data has appeared in the literature. The tables have been revised in this paper therefore to include these new systems, most of which are taken from Reference 3.