Report of Committee 11

Thermodynamics, Colloid Chemistry and Ion Exchange

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REPORT OF COMMITTEE 11

The topics assigned to this committee included thermodynamics, thermochemistry, phase equilibrium, gaseous state, colloid chemistry, surface chemistry, and ion exchange. In this section, topics have been divided into three categories: Ion Exchange, Thermodynamics (including thermodynamics, thermochemistry, phase equilibrium, gaseous state) and Colloid Chemistry (including colloid and surface chemistry). The material reported is based on returns from questionnaires covering each of the three parts, the general surveys conducted by the Chemical Institute of Canada, interviews, and personal knowledge. Activity in these fields in Canada has been judged in two ways: First, on the number of graduate students performing research in these areas in Canadian Universities[1], as shown in Table 1. Second, on the research expenditures for universities and research institutes, governmental laboratories, and industry, as shown in Tables 2, 3 and 4, respectively; these data were obtained from the general survey of this report.

The pertinent point of Tables 1 to 4 is that research in thermodynamics, ion exchange, and colloid chemistry is small. Of all the graduate students in departments of chemistry and chemical engineering, Table 1, 2.9% were performing research in thermodynamics, 1.8% in colloid chemistry, and 0.3% in ion exchange. Research expenditures in universities and research institutes, Table 2, were given only for the total of activities of Committee 11, and this amount is only 2% of the total research

1) Graduate Students at Canadian Universities in Science and Engineering, 1967-1968, National Research Council, Ottawa, January 1968.

TABLE 1

Graduate Students Performing Research in Thermodynamics, Colloid Chemistry, and Ion Exchange in Canadian Universities

UNIVERSITY	CHEMISTRY			CHEMICAL ENGINEERING			
	Thermo-dynamics	Colloid Chemistry	Ion Exchange	Thermo-dynamics	Colloid Chemistry	Ion Exchange	Total
Alberta (Calgary)	2						2
Alberta (Edmonton)				4			4
British Columbia	1	2		1	1		5
Carleton		1					1
Laval				2			2
McGill	4	1		1	1		7
McMaster					2		2
Manitoba	6						6
Memorial		2					2
Montreal	8						8
New Brunswick				2	1		3
Nova Scotia Tech				1	1		2
Ottawa				5	1		6
Queen's	1	5		2			8
Saskatchewan				1			1
Sherbrooke	1	1					2
Simon Fraser	1						1
Sir George Williams	1						1
Toronto		5		2	2	3	12
Waterloo	2	3	1		3	1	10
Western Ontario	1	1					2
Windsor	4						4
	32	21	1	21	12	4	91
Total number of graduate students	1403			451			1854

TABLE 2

Research in Universities and Research Institutes

1. <u>Operating Expenditures</u> (in thousands of dollars)

	Operating Expenditures	Major Equipment	Major Installations	Total
Thermodynamics, Colloid Chemistry and Ion Exchange	423.0[a)]	59.0	0	482.0
Total of all C.I.C.'s areas	20,774.0	4063.0	448.0	25,~~285.0~~

2. <u>Manpower</u> (in man years)

	Academic	Postdoctoral fellows	Graduate Students	Technicians	Total
Thermodynamics, Colloid Chemistry and Ion Exchange	25	15	58	8	106
Total of all C.I.C.'s areas	1042	378	2178	598	4205

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a) The operating expenditures were divided as follows: Basic research ~~98.6%~~
Applied research 1.3%
Development 0.2%

TABLE 3

Research in Governmental Laboratories

(CIC Survey Data – Section 16.)

1. Operating Expenditures (in thousands of dollars) (Table [illegible] – Section [illegible])

	FEDERAL				PROVINCIAL			
	Basic	Applied	Develop-ment	Total	Basic	Applied	Develop-ment	Total
Colloid Chemistry	30.0	60.0	30.0	120.0	0	0	(25.0)[a]	(25.0)
Ion Exchange	0	0	0	0	0	0	0	0
Thermodynamics	~~202.0~~ 252.0	90.0	0	~~292.0~~ 342.0	0	0	0	0
	~~232.0~~ 282.0	150.0	30.0	~~412.0~~ 462.0	0	0	(~~250.0~~ 25.0)[a]	(25.0)

Total of all research in governmental laboratories = ~~24,433~~ 24,736.

2. Manpower (in man years) (Table 16 – Section 15)

	Ph.D.'s	BS & MS	Technicians
Colloid Chemistry	7[b]	0	5[b]
Ion Exchange	0	0	0
Thermodynamics	13	0	5
	20	0	10

a) Two projects on soil chemistry which were classified as part of Committee 16, Agriculture and Food Chemistry. Part of this fund could probably be classified as ion exchange.

b) Includes 1 Ph.D. and 2 Technicians involved in soil chemistry, see footnote a.

TABLE 4

Operating Expenditures

Industrial Research (in thousands of dollars)

Table 2.6, CIC Data — Section 18.

	Basic	Applied	Development	Total
Thermodynamics, Colloid Chemistry, and Ion Exchange	128.7	66.8	1.7	197.2
Total of all Industrial Research	8,299.0 8,299.0	40,620.7 ~~40.294.0~~	42,511.8 ~~42,211.0~~	91,431.5 ~~90,803.1~~

funds in this category. Graduate students reported in Table 2 are substantially lower than those reported in Table 1. This discrepancy results from classifying research by commodity and discipline. For example, research in colloid chemistry or thermodynamics may have been classified as Pulp and Paper, Fuels, etc. In governmental laboratories (Table 3) 0.59% of the total effort is devoted to colloid chemistry and 1.2% to thermodynamics. For industry, basic research in the areas of Committee 11 comprises 1.6% of basic industrial research, but total research under Committee 11 is only 0.2% of the total of industrial research (Table 4).

As mentioned in the last paragraph, a substantial fraction of research assignable to Committee 11 may be classified in terms of commodities and the numbers reported may be low by a factor as large as 2 or 3. Nevertheless, the reader may apply any reasonable factor to the data of Tables 2 to 4, and still conclude that the research effort in thermodynamics, colloid chemistry and ion exchange is relatively small.

THERMODYNAMICS

Thermodynamics provides basic information for chemistry, chemical engineering, and other fields of science and engineering, such as the energetics of physical and chemical processes, the equilibrium constants of chemical reactions, and the properties of real gases, gaseous mixtures, and solutions. The usefulness of present thermodynamics is derived from a vast heritage of careful measurements and methods derived for approximating thermodynamic quantities with moderate accuracy. Nevertheless, the chemist or chemical engineer frequently finds that the desired data for relatively simple molecules have not been determined. A modern technological society should make at least a modest, concerted effort to increasing the store of thermodynamic data as well as developing new experimental procedures and methods of correlating data. Canadian contributions to thermodynamics have been relatively small except for a few excellent researches of the National Research Council.

Currently there are about 15 principal investigators active in thermodynamics and their staff including graduate students total about 50. More than half of the principal investigators have been in the field less than 10 years and one-third are just beginning. In the year 1965-1966 no group had a budget as large as $50,000 and 3/4 of the groups operated on less than $20,000 per annum. The major source of funds were governmental agencies.

The most active field of investigation has been vapor-liquid equilibrium. These investigations yield the Gibbs free energy of mixing and information on other excess properties of solutions. Direct investigation of excess properties is another active area. In order of decreasing emphasis, research in thermodynamics may be placed in the following order:

1. Phase equilibria
   - A. Vapor-liquid
   - B. Solid-gas (vapor)
   - C. Solid-liquid
Liquid-liquid
2. Excess thermodynamic properties of solutions
3. Vapor pressure and/or P-V-T studies.
Correlation and prediction methods.

4. Equation of state.

5. Chemical reaction equilibria and pure component properties.

One factor limiting research activities in thermodynamics is the lack of trained personnel. Recently, for example, a professorship at a major university was not filled, because none of the applicants seemed to be qualified. Subsequently, a young Ph.D. was appointed at a lower level. Some types of research are not pursued because the equipment required is too expensive and complicated and would require a full-time technician to maintain it.

Suggestions made to this committee include:

1. A system of continuing and certain research grants to be established.
2. An immediate increase in financial support to university professors for training of the required personnel. Estimates of the increase required varied from 25 to 100%.
3. Research activities are spread thinly and seldom reach the critical size for optimum productivity. Establishment of a few centers of specialization seem desirable. The National Research Council represents one of these centres of specialization.

In addition to these recommendations a small continuing program should be devoted to increasing the store of thermodynamic data. These investigations are precise "data gathering" operations and are not suitable for academic work.

Colloid Chemistry is the study of systems whose properties are determined principally by the extent and nature of surfaces or interfaces. The subject for purposes of this survey includes, the basic science of dispersions and surface phenomena but exclude some specific and particular topics that are considered by other committees, such as chemisorption, heterogenous catalysis, electrode processes, corrosion, biological systems, flotation, chromatography, cloud physics, dialysis, paper electrophoresis, etc.

The significance of colloid chemistry is apparent across the whole spectrum of science and technology. Of the industries listed in the "CIC Classification of Industries 1967" almost all can be identified as involving processes dependent on surface phenomena and many of their products (dairy products, rubber, adhesives, paints, soaps, lubricants, inks) are colloidal systems. A contriubtion to the survey stated "....for pulp and paper, this is the most important sub-discipline in chemistry". Colloid and surface chemistry is no less important in other diverse fields: meterology, soil science, air and water pollution and purification, biophysics and tar sand exploitation.

In all of the major countries, interest in colloid chemistry has decreased sharply since about 1945[2)]. In many physical chemistry departments of universities this subject was replaced by courses and research in molecular structure and quantum chemistry. In a few instances colloid chemistry has reappeared but usually in chemical

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2) For the plight of academic work in colloid chemistry in the United States, c.f. the "Introduction" to Chemistry and Physics of Interfaces, American Chemical Society Publications, Washington, D.C., 1965, pp. vii-viii.

engineering departments. The lack of academic leadership and training seems to be the primary cause of the decline in colloid chemistry in the last 20 years. The data reported in Table 1 are somewhat misleading as more than half of the entries refer to work on physical adsorption.

The history of colloid and surface chemistry in Canada is a fragmented story. Threads can be traced through wartime charcoal sorption and chemical warfare studies and several men prominent in the field have this background. However, activity in this field has apparently arisen at various times and places as demand and individual interest have developed. The research activity in Canada appears to be thinly spread over all the aspects of the subject.

Consensus as to significantadvances and neglected areas is not apparent in the replies to our questionnaires. This is taken as a further indication of the diversity of the field and of the viewpoints and knowledge of the respondents. Two subjects (adsorption and flocculation) in fact appeared as areas of significant advance and as areas of neglect. Few subjects in either list were mentioned by more than one respondent.

All consultants felt that colloid chemistry was a neglected field and that expansion was warranted. Several felt that expansion was imperative particularly as it pertains to problems in biological science and in air and water pollution.

The factors hampering research in colloid chemistry centre on lack of trained personnel while lack of financial support is secondary. Lack of equipment or information retrieval does not play any role while lack of communication and community of interest does contribute.

The reason for the lack of research activity in the field and the lack of trained personnel is attributed to the lack of emphasis given the subject in Canadian universities. A survey of the calendars of 28 Canadian universities indicate that only 9 chemisty departments have courses at the graduate or senior undergraduate levels that are wholly devoted to Colloid and Surface Chemistry and only 4 more describe advanced courses which indicate that the topic is included. Almost all the respondents recognized this deficiency and the methods suggested for expanding activity in the field included the establishment of advanced courses in the universities.

A strong representation was made for the establishment of one or more active centres of specialization in surface science. These centres would be located at a university and would function by co-operating with industry and have government support. Such institutes would become a source of trained personnel, could actively pursue projects of long term interest to industry and provide a focus for communication for Canadian researchers in the field. The Department of Physical Chemistry at the University of Bristol and the Institute of Colloid and Surface Science at Clarkson College, Potsdam, New York were cited as examples of successful co-operative ventures in this field. The Polymer Institute of the Chemistry Department at McGill was also mentioned as a pattern for establishing a specialized interest group.

Ion Exchange is closely related to colloid chemistry and principles governing ion exchange are similar to those of other diffusional mass transfer operations. Predictable reversibility of the reaction is probably its most unusual feature. The structure and properties of ion exchange materials, equilibria and reaction kinetics are often not particularly well known, and have not been studied as thoroughly as the overall process. The ion exchange process is sufficiently well accepted that it has been classed as a unit operation for some years, along with distillation, absorption, solvent extraction, etc.

Ion exchange resins were first prepared in 1935 and practical materials of the type currently used date from 1944. Because of their durability and versatility, the ion exchange resins have replaced inorganic exchangers.

The major application of the ion exchange process is still the treatment of natural water by one of the standard methods. Countless procedures for separating or concentrating ions selectively using ion exchange materials and techniques are available, but very few are in commercial operation in Canada; one exception is the concentration of uranium salts as part of ore refining. In the United States and in Europe some of these specialized techniques have been successfully developed to a commercial size to recover valuable trace metals from rinse waters, to de-ash sugar solutions, in the purification of fine chemicals, to remove low levels of radioactive contamination from cooling waters or waste water, organic chemicals separations using ion exclusion and elution, and to de-salt brackish water. Ion exchange processes seem to have a large potential in Canada in separation valuable metals in ore refining and in an attack on the water pollution problems of the Great Lakes.

The universities in Canada are carrying on some research on basic ion exchange chemistry, and also on the development of existing ion exchange techniques, but activity is small. Some interesting work is in progress on semi-permeable membranes and a better understanding of the parameters of this process could eventually result in economical de-salting of sea water.

Very few industrial laboratories have indicated any work being carried out in ion exchange even though most of their industrial operations have used such processes for some time. Further, there were few suggestions that investigations were even planned in the field of ion exchange, and no opinion that beneficial results could be expected from such work.

Ion exchange materials proper embrace a very small and specialized section of polymer chemistry, and they are not produced or manufactured in Canada. Accordingly commercial investigations into the basic materials or into their improvement and modification is not carried out here. About 95% of the ion exchange equipment is used for treatment of natural water, and the remainder are diverse specialized operations developed by parent organizations with investigative facilities outside Canada.

Ion exchange has so many attractive possibilities for the chemical industry that sundry specific investigations, usually short term, will always be in progress. However, major studies of theoretical or developmental nature have not been undertaken by research or development groups in universities, government, or industry. The modern era of ion exchange is, however, only twenty years old, and the present philosophy may change in the future.

Thus at present there is little research and development in ion exchange, and few are trained in this area. Despite its usefulness, the field is a minor branch of colloid chemistry or chemical engineering. Possibly in this area the purchase of "know-how" and complete units is economically sound. Nevertheless, some continuing research in this field seems desirable in chemical engineering departments or as a part of colloid chemistry in universities or research institutes.

SUMMARY AND RECOMMENDATIONS

Thermodynamics is a basic subject for all of science and engineering, and is particularly useful in chemistry and chemical engineering. Research in this field in Canada was considered to be less than adequate. Lack of trained personnel, of specialized equipment and operating funds, and of community of interest are the principal contributors to the present situation.

Colloid chemistry is an essential discipline for many of Canada's important industries, and small to modest research activity is found in industrial and governmental laboratories and in research institutes. In Canada and elsewhere, courses in colloid chemistry and research have nearly disappeared at universities. The lack of academic leadership and training is the most serious difficulty in this field, and the shortage of trained personnel outweighs all other problems, such as the need for additional funds and specialized equipment.

Ion exchange is a small specialized subject related to colloid chemistry and chemical engineering. Except in the treatment of natural water, its potential has not been fully realized by Canadian industry. The very small research effort is widely scattered in industry and university, and in most instances will not lead to any overall expertise in this field. Possibly the purchase of foreign "know-how" and processes is economically sound in this small specialized field, yet Canada should have a knowledgeable group of chemists and engineers who are conversant with recent developments and their application to Canadian problems.

The following recommendations are made:

A. Thermodynamics

1. The number of individuals trained in thermodynamics should be increased, and this can be accomplished by increased financial support to university professors and funds to purchase and maintain specialized equipment.
2. The establishment of two or three centers of specialization in universities or governmental laboratories to promote thermodynamic research.
3. The establishment in a governmental laboratory or a research institute of a small continuing program of determining and publishing thermodynamic data.

B. Colloid Chemistry

1. The establishment at one or more universities of centers of specialization or research institutes concerned with colloid chemistry. Training of personnel would be an important objective of these groups.
2. All universities should be encouraged to offer courses and research in colloid chemistry in departments of chemical engineering or applied chemistry if this subject can not properly be reintroduced in chemistry departments. Chairs

of colloid chemistry should be established at several universities.

C. Ion Exchange

1. Recommendations here are similar to those for colloid chemistry but with more limited objectives. One of the centers of specialization in colloid chemistry should have an expert in ion exchange. Courses and research in ion exchange should be provided in at least two or three chemical engineering departments.

Respectfully submitted by:

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