CUTTING-EDGE CHEMISTRY: SOME 19TH - CENTURY RUSSIAN CONTRIBUTIONS. A COMMENTARY

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The Nature of Scientific Discovery

[M. Kaji, "D. I. Mendeleev and the Concept of Chemical Elements"]

This presentation follows the "classic" paper of Bensaude-Vincent (1) rather closely, but with some additional points and emendations to her argument. One of the first points Kaji makes—that Mendeleev was ambivalent about the status of the atomic theory—can be related to what Bensaude-Vincent delineates as the "strict positivist tradition" to which he belonged. Kaji, however, give this philosophical context concrete scientific grounding in his reference to Mendeleev's interest in so-called "indefinite compounds" (solutions, alloys, silicates, etc.).

In the same and following sections Kaji explores the relationship of the writing of the textbook, *The Principles of Chemistry*, and the discovery of the periodic law. Here Kaji appears to emend Bensaude-Vincent most fundamentally. She was at pains to dispel the "myth of a sudden discovery," stressing that the genesis of the concept of the periodic law for Mendeleev was a slow one, going back to ca. 1860. As a kind of indirect evidence, she analyzed the structure of *Principles*, suggesting that its odd structure, with the setting forth of the periodic law deep into the work (at the end of the first part) was, in fact, in line with Mendeleev's pedagogical aims of moving from concrete chemical facts to the more abstract conception of elements arranged in the periodic table. She noted that the first part moved successively through consideration of water, air, carbon compounds, and common salt. The elements involved here (H, O, N, C, S, Cl) were to be heads of groups in the periodic table (with the exception of S). But S and Cl set the stage for what became systematic presentations pointing towards the periodic table: of the halogens, alkali metals, and alkaline earths. Then came the climactic presentation of the periodic law.

By contrast, Kaji at least implies something of a sudden discovery of this law and claims that one can see "when" it occurred through inspection of *Principles*. Examining the same first part of the textbook as Bensaude-Vincent, Kaji finds that the foci of the first part illustrate a pre-periodic conception of chemical "element" based upon *valency*. It was precisely at a particular point in the textbook (the chapter on heat capacity) that a disjunction occurred, with the discovery of the periodic law and the new conception of chemical element based on *atomic weight* and not on valency.

Continuing his analysis of the textbook (diachronically now), Kaji emends another assertion of Bensaude-Vincent: that Mendeleev never changed the presentation of his textbook. Kaji shows that extensive changes were made over the eight editions; however, he fails to make clear what the format for the first edition was. In his enumeration, the third edition (1877) seems to correspond most closely with his earlier outline of the work's structure

Despite these emendations to Bensaude-Vincent's analysis, there are fundamental agreements, most notably over Mendeleev's mature notion of elements as unchangeable entities, defined by atomic weight.

Science Across the Borders: National Patronage and Tradition vs. International Scientific Transfer

[R. E. Rice, "Hydrating Ions in St. Petersburg and Moscow; Ignoring Them in Leipzig and Baltimore"]

This paper deals with the reception of physical chemistry in Russia (or better, perhaps, the interaction between German and Russian theories of solution). Specifically, Rice recounts the vicissitudes faced by two Russian chemists, Kablukov and Kistiakovskii, in their espousal of physical chemistry, generally, and their attempts to reconcile the ionic theory and hydrate theory of solution. Regarding the latter, Mendeleev, who first set forth such a theory in Russia, plays as central (if more indirect) a role in Rice's paper as he does in Kaji's paper. Certainly Kablukov and perhaps Kistiakovskii (it is not clear from the paper) first become interested in the hydrate theory solution under Mendeleev's influence while studying at St. Petersburg University. Both also became enthusiasts for physical chemistry generally and arrange to take study leaves in Leipzig.

Upon their return to Russia, their stories diverge. Kablukov went back to Moscow University, where he was able to defend a dissertation, which Rice characterizes as "the first systematic discussion of the new physical chemistry in Russia." In it (and in his physical chemistry textbook of 1902), Kablukov suggested that the ion and hydrate theories of solution could be reconciled; however, he never produced the synthetic theory.

Kistiakovskii, who seems to have been much more determined to produce a synthetic theoretical explanation of solution than Kablukov, encountered great hostility toward physical chemistry in St. Petersburg and was effectively blocked from pursuing physical chemistry towards a degree or carrying out research there. There were clearly important local differences in attitudes towards physical chemistry in Moscow and St. Petersburg universities, which would merit some discussion. In particular, what role did Mendeleev play in all of this at St. Petersburg?

What does come clear is that, despite the efforts of two talented young chemists, physical chemistry did not readily take root and flourish in Russia. It would be interesting to compare and contrast its development in other "peripheries," such as the United States, for which we have an authoritative study by John Servos. In the US, there was much more receptivity because there was no equivalent of Mendeleev with an anti-ionic theory of solution, and because there was an industrial "market" for chemists trained in physical chemistry.

Chemistry and Industrial Context: Issues of Pure vs. Applied Chemistry

[N. M. Brooks, "Nikolai Zinin and Synthetic Dyes: The Road not Taken"]

This paper, as well as that by Lewis, deals with aspects of the important 19th-century chemical "school" at the University of Kazan'. In Brooks' paper a number of characteristics of Russian chemistry are highlighted: the role of state administrators in determining what kind of academic career a would-be scientist will have (and where it would be); the tradition of the fixed-term study leave for dissertation research in a western European center of scientific activity; and, most important of all, the attitude towards practical chemistry. Brooks' thesis seems to be that "Zinin's aversion to the practical use of his research" inhibited his development of work on the reduction of nitrobenzene to aniline into a broader program on aniline chemistry for industrial uses, as Hofmann was to do in the 1840s and 1850s. I am not completely convinced of this thesis, at least as sketched out here; it was, after all, quite some time—some 13 years—after Hofmann initiated his work on coal tar chemistry that the first aniline dye was produced. But if Brooks is correct that the aversion to practical chemistry was "a common feature of much Russian chemistry during the nineteenth century," it might well tie into Rice's story about physical chemistry, which could also be styled "the road not taken." Namely, both Brooks' thesis about the anti-practical orientation of Russian chemistry and Rice's about the lack of receptivity of physical chemistry in Russia may have wider industrial contexts (or, better, lack thereof).

This, in turn, impels me to call for more information on one point of Zinin's career highlighted in this paper: his assignment to the *kafedra* of technology at the University of Kazan' at the behest of the Curator of the Kazan' Education District, Count Musin-Pushkin. How did the position come about? About what was the professor expected to teach? How did he interact with the extra-university commercial and industrial sectors, and were these private or state-owned and operated?

The Nature of Research Programs

[D. E. Lewis, "The Beginnings of Synthetic Organic Chemistry:Zinc Alkyls and the Kazan' School"]

This paper is perhaps the closest exemplar of the theme of this session. Lewis delineates a clear-cut (and very distinguished) Kazan' research tradition, originating, perhaps, with Zinin, but getting its main impetus from Butlerov: the synthesis of alcohols from alkylzinc reagents. On the chemistry itself, I have nothing to add. But I do have questions concerning some of the contextual issues—issues common to some of the other papers as well.

The first and most obvious is the University of Kazan' itself. Both Lewis and Brooks emphasize its "fringe" location as "the easternmost university in Europe." Yet, early in the century, it had had Lobachevskii in mathematics and in the second half, the distinguished sequence of chemists whose work is detailed in Lewis' paper. My question is why: Was the success in the sciences here explicable simply in terms of fortuitously lucky interpersonal interactions, or should we also look for other reasons? A possible one (just from the inspection of Lewis' paper) concerns the place of chemistry in the curriculum at Kazan'. All these chemists came to Kazan' with other career goals; and, unlike Zinin, they were not "drafted" into chemistry by state officials but freely chose chemistry after being exposed to it in the course of their university studies. How did this come about? In another paper (2) Lewis noted (regarding Zaitsev) that "all students in the Faculty of Law were required to pass two years of chemistry in order to graduate." Markovnikov had also been a law student and, presumably, was attracted to chemistry by the same curricular path as Zaitsev (through Butlerov's lectures). Vagner, too, had switched from law to chemistry under the impact of Zaitsev's and Markovnikov's lectures. What was the intent of this requirement, and were there similar ones vis-à-vis chemistry for other faculties of study at Kazan'? Reformatskii had been a seminarian; but he, too, switched to chemistry after "encountering" Zaitsev at Kazan'.

Secondly, what were the laboratory research conditions at Kazan', and how had they developed in the era between Zinin and Zaitsev? In an earlier paper on chemistry at Kazan', Lewis noted (3) that Markovnikov "frequently bemoaned the backwater conditions under which Russian scientists worked;" yet Zaitsev appears to have developed a vigorous research group after Markovnikov left Kazan'. Rocke (4) has recently emphasized the importance of state subsidies to academic chemical laboratories in accounting for the contrasting development of German and French chemistry after 1840. What was the situation in Russia, particularly at the University of Kazan'?

Lastly—more an observation than a question—in the two papers by Rice and Lewis there is an interesting interaction—one might almost call it a dialectic—in the development of chemists, between their domestic and foreign mentors: Ostwald and (or *versus*) Mendeleev in the case of the physical chemists; Kolbe and Butlerov in the case of Zaitsev. This is quite different, I think, from the contemporary analog of American chemists' going abroad for advanced work: unlike Russia, there were no domestic giants whose mentorship could interact in this way with that found in the "high" centers of scientific research in Germany or France. Significantly, by 1875, the research leave for Vagner was in Russia itself, at St. Petersburg.

REFERENCES AND NOTES

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