Sabbatical Report: Heat Capacities, Refrigerators, and "Self-Charging" Batteries

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Three disparate topics in physical chemistry will be discussed.

1) The quantitative behavior of heat capacities of $N_2(g)$ and $F_2(g)$ at high temperature cannot be understood by resort to the equipartition theorem nor calculated with the usual closed-form expressions for the statistical mechanical molecular partition function. Because these molecules are much closer to their dissociation limits at these high temperatures, one must instead return to the fundamental definition of the partition function, taking into account the finite number of rotational-vibrational states as well as the centrifugal barrier due to rotational motion.

2) Within less than a century, refrigerators went from a luxury for the rich to an essential part of modern life, allowing the safe extended storage of food and more importantly, of life-saving medicines and vaccines. Recent developments in absorption refrigerators, including portable operation and use with passive solar-powered devices, will be briefly reviewed. The applications for areas of the world without developed electrical grids, and the possibility to save many lives, are very exciting. The absorption refrigerator seemingly paradoxically uses flame or other heat sources, instead of the more common vapor compression refrigerator, which requires high power gas compressors (pumps). Refrigerators are often characterized as heat engines "run in reverse" and so thermodynamic cycles for both heat engines and refrigerators will be discussed. The IcyBall, an absorption refrigerator sold during the 1920's and 30's in the United States, brought refrigeration to rural areas lacking both electricity and ice service. The IcyBall used no electricity and evokes a by-gone era of that old-fashioned Prairie know-how. Its operation will be detailed.

3) Are continuously self-charging batteries a possibility? We will briefly discuss a new research channel, thermally regenerative electrochemical cycles (TREC). Electrochemical cells (batteries) can be discharged at one temperature and, when depleted, their temperature can be changed, allowing the reverse reaction to become spontaneous with subsequent discharge at the higher temperature. The coupling of these cells to oscillating heat sources, such as, but not limited to, diurnal variations in sunlight, is contemplated.