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DIFFICULTIES IN INTERPRETING Alkali Metal Trends AT THE SENIOR CHEMISTRY LEVEL

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SUMMARY

Differences in alkali metal reactivity with water are often explained in terms of first ionisation energy trends in the Periodic Table. While a smooth trend exists for the first ionisation energy of the alkali metals with atomic number, such a trend is absent from the alkali metal activity series even though the basic reaction type, $M \rightarrow M^+ + e^-$, is the same. The reasons for the difference are explored in terms of the thermodynamics in each case and it is shown that differences in alkali metal reactivity with water are more appropriately explained in terms of the kinetics of the reactions.

BACKGROUND

Most students will leave high school having experienced at some stage the rather spectacular reaction between sodium and water. Senior Chemistry students will be aware that the vigor of such an alkali metal reaction with water increases as the atomic number of the alkali metal increases. That is, potassium reacts more vigorously with water than does sodium and sodium reacts more vigorously with water than does lithium. What is the reason for such a trend? Can one use the trend in first ionisation energies, shown in Table 1, to explain the trend in reactivity with water? Is it legitimate to say that potassium reacts more vigorously than sodium because less energy is required to remove its electron than is the case for sodium? Some chemistry textbooks imply that such a reactivity trend can be explained in terms of the trend in ionisation energies. Verma (1981, p35), for example, explains alkali metal reactivity this way: 'The ability to supply electrons makes the alkali metals very reactive. The larger the atom, the easier it is to remove the outer electron. The size of the atom increases with an increase in atomic number. Therefore the reactivity of the alkali metals also increases with increase in atomic number'.

THERMODYNAMIC DESCRIPTION

One of the difficulties associated with using ionisation energies to explain reactivity trends with water is that the ionisation energies refer to the element and ion in the gas phase whereas the reactivity with water is based on the element in the solid phase and the ion in the aqueous phase. Consider the standard enthalpy changes (ΔH^0) and standard free energy changes (ΔG^0) for the reaction

$$2M_{(s)} + 2H_2O_{(l)} \rightarrow 2M^+_{(aq)} + 2OH^-_{(aq)} + H2_{(g)}$$

as shown in Table 2. When the appropriate phase is used for the metal and its ion no smooth trend in energies, like that shown for first ionisation energy, is observed. It is therefore very misleading to use ionisation energy trends to explain reactivity trends of alkali metals with water. One of the reasons for there being no smooth trend in the data of Table 2 is due to the fact that as the ionisation energy of the element becomes more endothermic as shown in Table 1, the hydration energy of the ion becomes more exothermic as shown in Table 3. The combined effect of adding atomisation

TABLE 1.

FIRST IONISATION ENERGIES FOR THE ALKALI METALS, $M_{(g)} \rightarrow M_{(g)}^+ + e^-$

(Aylward & Findlay, 1994).

Alkali Metal, M	IE_1/kJ mol^{-1}
Li	526
Na	502
K	425
Rb	409

TABLE 2.

STANDARD ENTHALPY CHANGES (ΔH^0) AND STANDARD FREE ENERGY CHANGES (ΔG^0) FOR THE REACTIONS OF ALKALI METALS, $M_{(s)}$, WITH WATER, $H_2O_{(l)}$.

(Aylward & Findlay, 1994).

$M_{(s)}$	ΔH^0/kJ mol^{-1}	ΔG^0/kJ mol^{-1}
Li	-444	-426
Na	-368	-364
K	-392	-408
Rb	-390	-408

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TABLE 3.

HYDRATION ENERGIES FOR, $M^+_{(g)} + aq \rightarrow M^+_{(aq)}$, WHERE M^+ IS A CERTAIN ALKALI METAL ION.

(Aylward & Findlay, 1984).

M^+	$\Delta H^0_{hydration}$/kJ mol^{-1}
Li^+	-519
Na^+	-406
K^+	-322
Rb^+	-301

TABLE 4.

OXIDATION POTENTIALS FOR, $M_{(s)} \rightarrow M^+_{(aq)} + e^-$, WHERE M IS A CERTAIN ALKALI METAL.

(Aylward & Findlay, 1994).

M	E^0(volt)
Li	3.04
Na	2.71
K	2.94
Rb	2.94

TABLE 5.

MELTING POINT TREND FOR THE ALKALI METALS, M.

(Aylward & Findlay, 1994).

M	Melting Point/°C
Li	186
Na	97.8
K	63.6
Rb	38.9

energies for the alkali metals ($M_{(s)} \rightarrow M_{(g)}$ which becomes more endothermic as one goes from rubidium to lithium) to ionisation energies and hydration energies to give energies for, $M_{(s)} \rightarrow M^+_{(aq)} + e^-$, is a set of energies showing no smooth trend, a similar situation to that shown in Table 2. This lack of a smooth trend is also shown in the oxidation potentials for the alkali metals shown in Table 4. This is not surprising given the relationship, $\Delta G^0 = -FE^0$, between the standard free energy change, ΔG^0, Faraday's constant, F, and the redox potential, E^0. Remember though, that the ΔG^0 data in Table 2 refers to a different chemical equation from the data in Table 4 but the trends are similar for the same reasons. This explains why students commonly find it difficult to reconcile the smooth trend in Table 1 with the lack of a smooth trend in Table 4 although the reaction type, $M \rightarrow M^+ + e^-$, is similar.

KINETIC DESCRIPTION

What, then, explains the increased vigor of the reaction with water as one descends the group of alkali metals in the Periodic Table? The answer lies in the low melting points of the metals and the fact that the melting point decreases as one descends the group. See Table 5.

Shriver and Atkins (1999, pp286-287) explain the trend this way. "The vigor of these reactions is associated with the low melting points of the metals, because once molten a clean metal surface is more readily exposed and rapid reaction ensues". The exothermic reaction, with enthalpy changes shown in Table 2, provides enough heat to melt the metal and the lower melting point metals will more easily expose their surfaces than the higher melting point metals leading to potassium, for example, reacting more vigorously than sodium. The greater the surface area of metal exposed the greater the reaction rate.

CONCLUSION

Thus kinetics, not thermodynamics, should be used to explain relative reaction rates. It is helpful to remember that thermodynamics (energy considerations) gives us information about the *extent* of reaction but kinetics (surface area, concentration, temperature, catalyst) gives us information about the *rate* of reaction. The information in Tables 2 and 4 tells us that all the alkali metals have approximately the same strength as reducing agents. That is, they reduce water to hydrogen to about the same extent. The equilibrium constants, K (measures of extent), calculated from, $\Delta G^0 = -RT\ln K$, and $\Delta G^0 = -nFE^0$, are large and of a similar order of magnitude. In these equations, R is the gas constant, T is the absolute temperature, and n is the number of electrons in the half equation. However, as we know, the reaction rates increase as one uses a lower melting point metal because as the surface exposure of the metal increases more molecular collisions can occur every second. The role of kinetics and thermodynamics is a vital one that becomes increasingly important in tertiary level chemistry. Early exposure to this relationship through a common experimental example like that of the reaction between an alkali metal and water can enhance the students' appreciation of the role of energy and the collision model in chemistry and assist in the students' preparation for what becomes central in much of tertiary level chemistry.

References

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