Rate of Reaction of Hydrogen with Liquid Caesium: Recalculated Rates for Lithium and for Potassium

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The rate of absorption of H_2 by stirred liquid Cs to form CsH has been measured from 373 to 576 K, with starting pressures of 20 kN m^{-2}. The reaction obeys first-order kinetics and only becomes complicated by the dissociation pressure of CsH above 542 K. The apparent activation energy of the reaction is 42.4 kJ mol^{-1}. Previously reported rates for Li and K are recalculated and the rates are seen now to decrease in the order Li > Cs > K > Na, largely due to the activation-energy term in the Arrhenius equation. The fundamental difference in the rates is attributed tentatively to the differing strengths of the M–H (M = Li, Na, K, or Cs) bonds.

THE main stimulus to study liquid caesium chemistry stems from the unavoidable generation of long-lived radioactive ^{137}Cs in nuclear reactor cores and aspects of its partition between cover gas and fuel elements, and its deposition characteristics in liquid sodium coolant. The present work shows that H_2 reacts more rapidly with Cs than with Na, and therefore promises selective removal of Cs, but only under non-equilibrium conditions since NaH is the more thermodynamically stable product. The present work also augments the previous fundamental studies on Na,[1] K,[2] and Li,[3] and confirms the suspected view[3] that the simple reaction with H_2 does not follow the common pattern of increasing reactivity with increasing atomic number of the metal, but that Cs and Li react with H_2 at comparable rates.

EXPERIMENTAL

The apparatus (Figure 1) was constructred from Pyrex glass for ease of visibility rather than from steel,[2,3] but differed from the original glass version[1] in that a *single* pump duct carrying a larger current (50 A) between the poles of a stronger permanent magnet (0.5 T) was employed to draw the liquid metal from the reservoir and to inject a clean stream into the hydrogen above. Caesium (Kawecki–Berylco, 99.98%, 150 g) was melted without further purification from a storage cylinder into the reaction vessel under vacuum, care being taken not to contaminate the Teflon sealing rings of the greaseless tap. The vessel and magnet were mounted up to the tap in an air-oven controlled to ±1° at 523 K, and known volumes of H_2 (Air Products, 99.98%) were exposed to the circulating metal. The fall in pressure from 20 kN m^{-2} with time was followed by means of a mercury manometer and a pressure transducer. The reactive surface area of the metal was calculated as before[1] from the length and diameter of the jet, from the dimensions of the fan of metal striking the glass wall, and from the diameter of the pool of liquid metal below. Absorptions between 373 and 576 K were carried out in vessel I with one volume of Cs. They were subsequently repeated with fresh Cs in vessel II which was of similar design, but of different dimensions to obtain a different surface area of metal and a different gas volume. The solubility of CsH in Cs is low, rising to a mere 1.0 mol % H at 573 K[4] so that H_2 reacts essentially with a saturated solution, and the small amount of solid CsH so formed is swept to the side of the vessel by the circulating metal, and does not inhibit the metal–hydrogen reaction. Thus, several volumes of H_2 can react with the one volume of Cs.

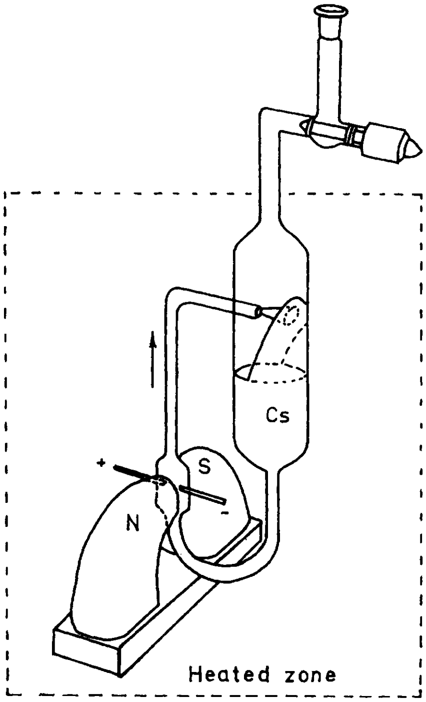


FIGURE 1 Apparatus

RESULTS AND DISCUSSION

Effect of Pressure.—The pressure generally fell smoothly from 20 kN m^{-2} to near zero with time. The rate of fall in pressure was directly proportional to the pressure in accordance with first-order kinetics, equation (1). This

$$-\mathrm{d}P/\mathrm{d}t = k_pP \text{ or } \ln P = k_pt + \text{integration constant} \quad (1)$$

is shown by the linear regions (which are slightly curtailed at low pressures for brevity in Figure 2) of typical $\ln P$ against t relationships for each of the two vessels, and in this respect Cs resembles Li, Na, and K. Above *ca*. 508 K, however, the pressure fell to measurably finite equilibrium values (Figure 2) due to the reverse dissociation process [equation (2)], and these increased with

$$CsH \rightleftharpoons Cs + \tfrac{1}{2}H_2 \quad (2)$$

increasing temperature (1.0, 1.9, and 3.3 kN m^{-2} at 542,

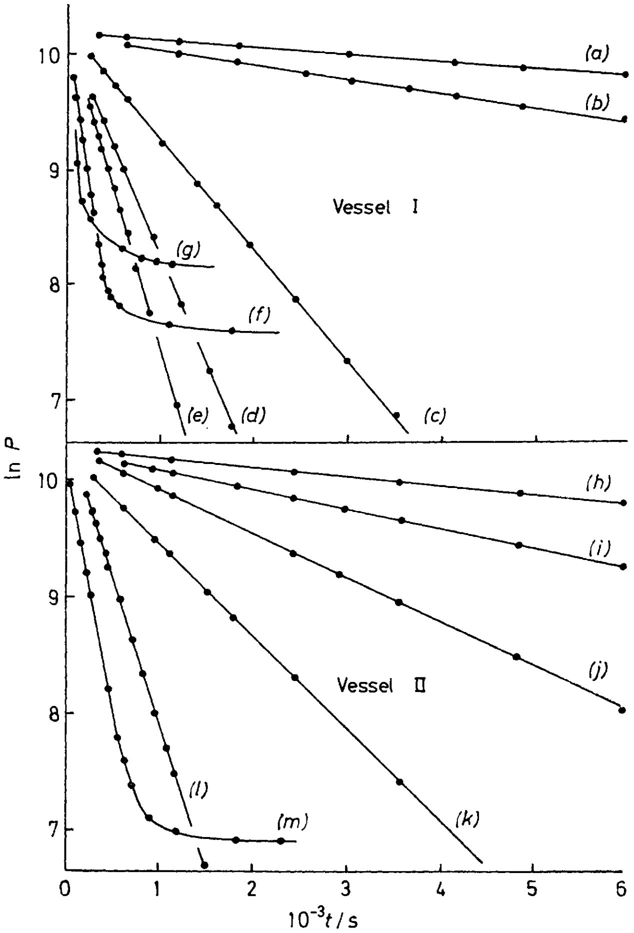


FIGURE 2 The effect of pressure (P/N m^{-2}) and temperature on the absorption of hydrogen by liquid caesium. Vessel I: (*a*) 377, (*b*) 397, (*c*) 476, (*d*) 507, (*e*) 520, (*f*) 559, and (*g*) 580 K. Vessel II: (*h*) 380, (*i*) 407, (*j*) 433, (*k*) 459, (*l*) 509, and (*m*) 542 K

559, and 576 K respectively) as expected.[5] Thus under the present conditions, Cs behaves like K but differs from Na and Li which have more stable hydrides giving correspondingly lower dissociation pressures which interfere less with the kinetics.

Rate Constant.—The slopes of the linear relationships (Figure 2) provide values of the rate constant, k_p, but this is more usefully converted into a constant, k, equation (3), ref. 5, which accommodates the different surface areas, volumes, V, and pressures, P, in the two vessels and also provides a method of comparing the rates of reaction of H_2 with different metals where $(\mathrm{d}V/\mathrm{d}t)_{\mathrm{STP}}$ is given by equation (4) and ν_1 and ν_2 are the

$$k = (\mathrm{d}V/\mathrm{d}t)_{\mathrm{STP}}\, S^{-1}\, P^{-1} \qquad (3)$$

$$(\mathrm{d}V/\mathrm{d}t)_{\mathrm{STP}} = (273/101\,325)[(\nu_1/T) + (\nu_2/298)]k_pP \qquad (4)$$

hot and cold gas space volumes (mm^3) respectively, above the metal of surface area S (mm^2). For vessel I, $\nu_1 = 102\,420$, $\nu_2 = 23\,330$ mm^3, and $S = 1\,476 \pm 85$ mm^2. For vessel II, $\nu_1 = 83\,140$, $\nu_2 = 24\,740$ mm^3, and $S = 1\,497 \pm 85$ mm^2. All of the values of k [mm$^3_{\mathrm{STP}}$ s^{-1} mm^{-2} (N m^{-2})$^{-1}$] obtained in this way are listed in Table 1. Strangely, the results using vessel I show more scatter within themselves than do those using vessel II, and the only explanation we can offer is that reproducibility improves with experimental expertise. Thus the results from vessel I carry no estimate of the accuracy but should be considered approximate only.

TABLE 1

Rate constants, k [mm$^3_{\mathrm{STP}}$ s^{-1} mm^{-2} (N m^{-2})$^{-1}$], for the Cs–H_2 reaction

T/K	10^8k_p/ s^{-1}	10^8k	T/K	10^8k_p/ s^{-1}	10^8k
373	5.3	3.0	507	191.5	98.0
377	6.8	4.0	507	153.0	78.0
380	7.9	4.3 ± 0.3 *	507	154.3	79.0
381	7.4	4.0 ± 0.3 *	507	138.2	71.0
397	13.2	8.0	508	255.6	113.5 ± 6.1 *
407	17.1	8.8 ± 0.5 *	509	244.3	108.3 ± 6.0 *
407	17.1	8.8 ± 0.5 *	520	286.0	144.0
421	13.8	8.0	520	267.8	135.0
433	37.7	18.7 ± 1.1 *	542	460.6	195.9 ± 12.0 *
433	35.1	17.4 ± 1.1 *	542	487.3	207.3 ± 12.0 *
459	84.3	40.1 ± 2.4 *	559	671.1	320.0
459	82.2	39.1 ± 2.4 *	559	671.1	320.0
476	128.7	69.0	580	694.4	325.0
476	77.5	41.0	580	878.0	411.0
476	94.7	50.0			

* Asterisked values for vessel II, others for vessel I.

Effect of Temperature.—The rate increased exponentially with increasing temperature thereby conforming to the Arrhenius relationship, equation (5). A straight line

$$k = A \exp - (E^{\ddagger}/RT) \text{ or } \ln k = \ln A - (E^{\ddagger}/RT) \qquad (5)$$

(method of least squares) drawn through a plot of ln k against $1/T$ of the more reproducible results gives a slope and hence a value of the apparent activation energy, $E^{\ddagger}$, of 42.4 kJ mol^{-1}. This is significantly greater than that (28.8 kJ mol^{-1}) obtained using static Cs over the range 323—347 K.[5] A comparison of activation energies (kJ mol^{-1}) for the reaction of H_2 with the alkali metals under dynamic conditions shows that they increase in the order Cs(42.4) < Li(52.8) [3] < K(66.5) [2] < Na(72.4,[1] 69.8 [6]).

Recalculated Rates for Lithium and Potassium.—Errors were made when laboratory units were converted into SI units for the rate constants for the reaction of H_2 with Li [3] and K,[2] but the non-SI units for Na–H_2 (ref. 1) still stand. The corrected values (Table 2) are necessary for comparisons between the various alkali metals. The rates do not fall precisely in the order shown by the activation energies due to a significantly smaller A value for Cs;

TABLE 2

Corrected rate constants, k [mm$^3_{\mathrm{STP}}$ s^{-1} mm^{-2} (N m^{-2})$^{-1}$], for the Li–H_2 and K–H_2 reactions

Lithium		Potassium	
T/K	10^7k	T/K	10^7k
490	9.17 ± 0.46	483	0.47 ± 0.02
517	14.94 ± 0.74	513	1.34 ± 0.07
530	22.60 ± 0.13	533	1.91 ± 0.09
543	28.96 ± 1.45	545	2.88 ± 0.14
568	47.14 ± 2.36	568	5.00 ± 0.25
		588	8.52 ± 0.43
		606	11.88 ± 0.59

thus at 523 K, for example, the rates (10^7k) decrease in the order Li(18.8) > Cs(14.6) > K(1.64) > Na(0.25). Nevertheless, the differences in the activation energy are largely responsible for the observed trend in rates as illustrated by the relative contributions of $E^‡$ and A to k in Figure 3. The ln A factor [equation (5)] makes a minor and nearly constant contribution to ln k and the trend in the larger $E^‡/RT$ values parallels the trend in ln k. No single property of the alkali metals follows precisely this trend in $E^‡$, be it ionization energy, work function, sublimation energy, or formation enthalpy of MH which all change fairly regularly with increasing atomic number so that the reason for the observed order is not immediately obvious. The possibility that this is due to the relative availability of empty metal *d* orbitals carries little conviction since ultimately electron transfer occurs from M to H to form H^- rather than *vice versa*. A clue is provided, perhaps, by assuming that $E^‡$ depends upon the simultaneous making of the surface M–H bond and breaking of the M–M and H–H bonds (see below) so that the departure from regularity is attributed solely to variations in the strength of the isolated surface M–H bonds. The chemisorbed bond energy has been likened to the bond energy of the gaseous molecule in specific cases, *e.g.* NiH(g),[7] so that equation (6) represents the adsorption process for which the heat of chemisorption, ΔH_c, is E(M–H)(g) − E(M–M) − $\frac{1}{2}E$(H–H)(g). It has been suggested that E(M–M) is approximately one sixth of the sublimation energy,[7] and using latent heats of vaporization[8] of 158.4, 107.4, 87.8, 85.3, and 78.6 for liquid Li, Na, K, Rb, and Cs respectively, and a value of 433.0 kJ mol^{-1} for E(H–H), combined with values[9] of E(M–H)(g) of −237.8, −200.6, −183.1, −175.6, and −194.8 kJ mol^{-1} for Li, Na, K, Rb, and Cs respectively, the calculated heat of adsorption, ΔH_c, is as shown by the parabola (broken line) in Figure 3. The heat of adsorption is least positive for Li (which forms strongest covalent bonds), followed by Na and Cs (which forms strongest ionic bonds) which are very close. The strength of the M–H bond goes some way, therefore, towards explaining the low activation energies and consequent fast rates for Li and Cs, but does not adequately account for the slow rate for Na.

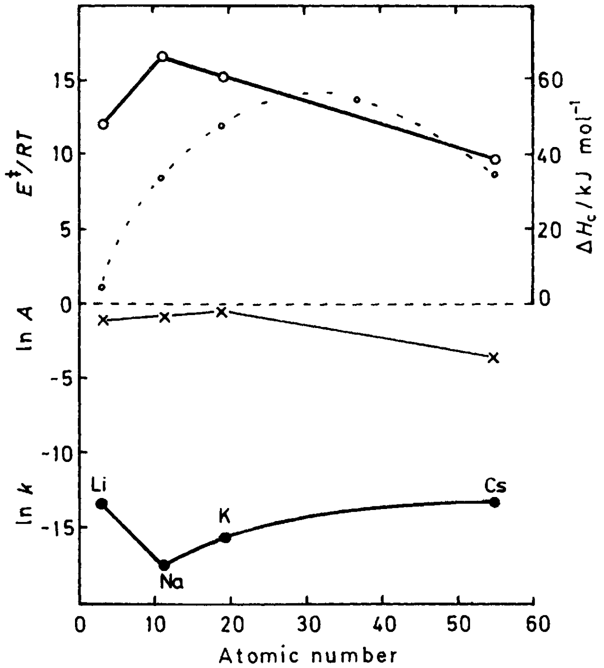
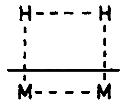


FIGURE 3 Contributions from $E^‡$ (○), A (×), and k (●) to the equation ln k = ln A − ($E^‡/RT$) for the alkali metals; (– – ○ – –) heat of chemisorption, ΔH_c



$$\underset{\text{surface}}{E(\text{M–M})} + \tfrac{1}{2}E(\text{H–H})(\text{g}) \longrightarrow [E(\text{M–H})(\text{g})] \longrightarrow \underset{\text{surface}}{E(\text{M–H})} \quad (6)$$

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