Differential kinetic method of analysis for the determination of mixtures of certain nitrocompounnds using Vanadium (III) sulphate as reagent

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INTRODUCTION

Vanadium and its compounds have occupied a dominant position in modern science and technology because of their versatile and diverse chemical, mechanical and electrical properties. The chemical characteristics associated with vanadium and its compounds are the major causes of their use in chemical industries as catalyst and redox agents in the synthesis of a variety of compounds of specific and selective character. Its thermo mechanical properties have been utilised in the field of engineering and technology for the production of many alloys and refractories of specific quality. The electrical properties of the metal have been explored by the workers in the manufacture of many electrical and electronic devices.

RESULTS AND DISCUSSION

The stoichiometry of the reduction of nitrocompounds by vanadium (III) has been discussed.

$$R\text{-}NO_2 + 6V^{3+} \longrightarrow R\text{-}NH_2 + 6VO_2^{+} + 4H^{+}$$
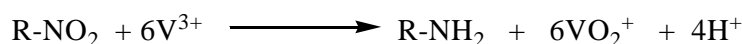
Vanadium (III) quantitatively reduces the nitrocompounds to the corresponding amines hence the stoichiometry is 1:6, which involves a six-electron change. The kinetic studies are carried out under the second order stoichiometric conditions so that the following differential equation could be used

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where a = initial concentration of nitrobenzene, b = initial concentration of vanadium (III)

Separating the variables and integrating

$$k_t = 1/(b-6a)]\ in\ a(b-6x)\ /\ b(a-x)$$

The plot of In a(b-6x) / b(a-x) vs time (t) is a straight line passing through the origin, indicating the first order dependency with the concentration of vanadium(III) and nitrobenzenes. From the slope, k the rate constant is computed.

The kinetics of vanadium (III) reduction of nitrobenzenes was investigated under varying concentration of [V(III)] and [H_2SO_4]. The effect of temperature is also studied at three different temperatures for the activation parameters and thermodynamic parameters, which are computed, from Arrhenius and Erying plots. The results are presented in table **5** & **6**.

Table-1: A few important minerals of vanadium

Name	Approximate formula
Patronite	$V_2S + nS$
Bravolite	$[Fe,Ni,V]S$
Salvanite	$3Cu_2SV_2S$
Davidite	$[Fe,U,V\ Cr,ReTiO_3$
Roscolite	$2K_2O_2Al2O_3[Mg\ Fe]O$ $3V_2O_5\ IOSiO2LiH_2O$
Carnolite	$K_2O,\ 2V_2O_3V_2O_53H_2O$
Vanadinite	$Pb_5(VO_4)_3C1$
Descloizite	$4[Cu,Pb,Zn]O\ V_2OH_2O$
Cuprodescloizite	$5\ [Cu,Pb]O,\ [V,As]_2O_52H_2O$
Titani ferous magentite	$Fe0,\ TiO_2,\ FeO[Fe,V]O_2$

Table-2: Thermodynamic data for vanadium at 298 K

Substances	AH0f	AGo f	S°	Reference
	(k J mol^{-1})	(k J mol^{-1})	(J K mol^{-1}	
V(s)	0	0	28.4512	21
V(g)	0.5146×10^3	0.4686×10^3	182.2132	20,21
V^+(g)	1.1673×10^3			
V^{2+}(g)	2.5439×10^3			
V^{3+}(g)	5.1087×10^3			
V^{4+}(g)	9.7906×10^3			
V^{5+}(g)	16.0164×10^3			
V^{2+}(aq)	-0.2259×10^{-3}	-0.2176×10^3	-0.129×10^{-3}	59
V^{3+} (aq)	$-.2594 \times 10^{-3}$	-0.2423×10^3	-0.230×10^{-3}	53
VOH^+ (aq)		-0.4226×10^3		47
VO^+ (aq)		-0.4017×10^3		47
$V0^{2+}$ (aq)	-0.4870×10^3	-0.4469×10^3	-0.133×10^3	25
$VOOH^+$ (aq)		0.6569×10^3		48
$(VOOH)_2^{2+}$(aq)		-1.3305×10^3		48
$VOSO_4$ (aq.ion pair)		-1.2050×10^3		
$V0^{2+}$ (aq)	-0.6498×10^3	-0.5874×10^3	0.0410×10^3	40,41

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VO(s)	-0.4318×10^3	-0.4042×10^3	0.0389×10^3	20
V_2O_3(s)	-1.2188×10^3	-1.1393×10^3	0.9883×10^3	20
VO_2(s)	-0.7138×10^3	-0.6594×10^3	0.0515×10^3	20
V_6O_{13}(s)	-4.4560×10^3	-4.1087×10^3	0.3347×10^3	25
V_2O_5 (s)	-1.5506×10^3	-1.4200×10^3	0.1309×10^3	20
V_2O_5-H_2O (s)	-1.8451×10^3	-1.6569×10^3	0.1715×10^3	20
VC_{12} (s)	-0.4561×10^3	-0.4100×10^3	0.0970×10^3	20
VBr_2 (s)	0.3598×10^3	-0.3389×10^3	0.1129×10^3	20
VI_2 (s)	-0.2510×10^3	-0.2468×10^3	0.1339×10^3	20
VCI_3	-0.5812×10^3	-0.5121×10^3	0.1309×10^3	20
VBr_3 (s)	-0.4435×10^3	-0.2678×10^3	0.1674×10^3	20
VI_3 (s)	-0.2719×10^3	-0.2678×10^3	0.184×10^3	20
VF_4 (s)	1.3431×10^3	-1.2510×10^3	0.1255×10^3	25, 37
VI_4 (g)	-0.1297×10^3			51
VF_5 (I)	-1.4728×10^3	-1.3682×10^3	0.1883×10^3	37
VF_5(g)	-1.4267×10^3	-1.3639×10^3	0.3259×10^3	38
$VOCI_3$ (I)	-0.7364×10^3	-0.6736×10^3	0.2552×10^3	23
$VOCI_3$ (g)	-0.6987×10^3	-0.6610×10^3	0.3435×10^3	20
$VOSO_4$ (s)	1.3058×10^3	-1.1690×10^3	0.1334×10^3	20
NH_4VO_3 (s)	-1.0531×10^3	0.8883×10^3	0.1406×10^3	25
$NaVO_3$ (s)	1.1459×10^3	1.0644×10^3	0.1138×10^3	25,26
Na_3VO_4 (s)	-1.7564×10^3	1.6368×10^3	0.1894×10^3	26
$Na_4V_2O_7$ (s)	-2.971×10^3	-2.7200×10^3	0.3184×10^3	25

Table -3: Second order rate constants for the reduction of Nitrobenzene by vanadium (III) sulphate

[H₂SO₄] = 0.05 mol.dm⁻³   Temperature = 301 K
[Na₂SO₄] = 2.00 mol. dm⁻³

[V (III) x 10⁻² (mol.dm⁻³)	[NB] x 10⁻³ (mol.dm⁻³)	K x 10⁻⁴ (dm⁻³. Mol⁻¹ s⁻¹)
1.5	4.0	2.039
2.0	4.0	2.649
2.4	4.0	3.526
3.0	4.0	4.149
2.4	1.0	0.731
2.4	2.0	1.676
2.4	3.0	1,513

Table - 4: Second order rate constants for the reduction of Nitro benzenes by vanadium (III) sulphate

[H₂SO₄] = 5.0 x 10⁻² mol.dm⁻³ Temperature = 301 K
[Na₂SO₄] = 2 mol.dm⁻³

[V(III) x 10⁻² mol.dm⁻³	[Nitro Comd] x 10⁻³ mol.dm⁻³						
1.498	4.00	1.0655	1.2420	1.5020	2.9800'	12.815	6.1486	19.470
1.998	4.00	1.3586	1.4868	1.8873	3.7033	10.003	8.5362	17.401
2.400	4.00	1.5413	1.9142	2.3334	4.6133	9.9983	10.800	15.319
2.998	4.00	2.1835	2.4303	3.3351	5.3613	4.3301	13.330	9.1497
2.401	1.00	0.4263	0.5001	0.9035	1.3333	2.670	3.0118	4.3330
2.401	2.00	0.9808	0.9466	1.8690	2.5363	5.3510	5.7016	9.1663
2.401	3.00	1.2480	1.3750	2.6641	3.3335	8.3466	8.5166	14.420

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Table - 5: Effect of sulphuric acid concentration and temperature on 1the reduction of nitrobenzene by vanadium (III) sulphate.

[V(III)] = 2.40 x 10^{-2} mol.dm^{-3} T_1 = 301 K
[NB] 4.0 x 10^{-3} mol.dm^{-3} T_2=305 K [Na$_2$ SO$_4$] =2 mol.dm^{-3}

[H$_2$SO$_4$] x 10^{-2} mol. Dm^{-3}	K$_{1obs}$ x 10^{-4} (dm^3 mol^{-1} s^{-1})	K$_{2obs}$ x 10^{-4} (dm^3. Mol^{-1} S^{-1})
2.00	4.535	5.002
4.00	3.688	4.622
5.00	3.526	4.545
6.00	3.539	4.491

Table -6: Effect of sulphuric acid concentration and temperature on the reduction of nitrobenzenes by vanadium (III) sulphate

[V(1I1)] = 2.401 x 10^{-2} mol.dm^{-3} [Na$_2$SO$_4$] = 2 mol.dm^{-3}
[Nitro Compound] = 4.0 x 10^{-3} mol.dm^{-3}

[V(III)] X10^{-2} mol.dm$^-$	[Nitro Compd] x 10^{-3} mol. dm^{-3}	ONT	PNB	PNT	ONBA	PCNB	MNBA	MCNB
2.0	301.00	3.3103	3.3918	3.5255	6.6493	15.765	14.825	24.833
4.0	30.1.00	2.8145	2.8918	3.9098	6.0326	15.393	13.858	23.688
5.0	301.00	1.5413	1.9140	2.3336	4.6131	9.9983	10.800	15.319
6.0	301.00	1.0025	1.3820	1.6650	3.3800	7.8733	7.3983	7.7481
7.5	301.00	0.6650	0.4913	1.2463	2.3315	4.1483	4.9202	5.5382
5.00	295.00	0.5831	1.2157	1.9308	3.0866	7.5226	6.4481	12.702
5.00	305	2.0830	2.4973	3.8633	6.150	15.533	12.986	22.097
5.00	310	3.2485	3.9996	6.8666	9.8316	21.332	14.665	30.832

Table - 7: Results of the analysis of the mixtures of nitrobenzenes via differential kinetic method

Composition of the mixtures

	COMPONENT-1	COMPONENT-2
1 MIXTURE-A	NB	ONBA
2 MIXTURE-B	NB	MNBA
3 MIXTURE-C	NB	PCNB
4 MIXTURE-D	NB	MCNB

Percentage of component-1 in the mixture

	Mixture A	Mixture B	Mixture C	Mixture D
Present	**Found**			
20	19.55	19.80	20.25	20.42
35	34.62	35.22	35.20	34.88
50	49.80	50.34	50.42	50.20
65	65.22	65.20	65.55	65.35
80	80.48	80.62	80.68	80.55

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