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SOLVENT FLUCTUATION IN THE THEORY OF ELECTRON TRANSFER REACTIONS IN SOLUTION

By

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Abstract

An examination has been made of the relative contributions of long range interactions of ions with solvent librators (continuum model) and thermally activated vibrational modes (bond stretching).

Plots of $\Delta G^{\neq}$ (continuum) $-\Delta G^{0}$ show that the range of $\Delta G^{\neq}$ calculated from the continuum theory is not consistent with the range of experimental values of $\Delta G^{\neq}$. A plot of $\Delta G^{\neq}$ (continuum) $-\Delta G^{\neq}$ (expt) shows a correlation of <0.5, $\Delta G^{\neq}$ (stretch) $-\Delta G^{\neq}$ (expt) of 0.7 and $\Delta G^{\neq}$ (stretch+continuum) $-\Delta G^{\neq}$ (expt) of 0.9. Considering only ions with big organic ligands does not improve the correlation of the continuum model with experiment.

Thermal activation of ion-ligand vibrators contributes about 2/3rds of the activation energy of redox reactions in solution. A contrary result can be obtained if the image contribution in the electrode case is removed and inappropriate force constants are used.

Introduction

In the continuum, solvent fluctuation model[1-5], the activation energy for electron transfer reactions in solution arises as a fluctuation of the energy of ions originating from their electrostatic interaction with the field of the librating solvent dipoles, *outside* the inner solvation sphere of the reaction species. Vibrational modes of interaction of the ion and the inner solvent sheath are postulated as *not* contributing to the activation of ions in simple redox reactions, proton discharge, *etc.*[6,**] On this model, theoretical relations have been given[6] for the free energy of activation of charge transfer reactions, and their dependence upon the free energy of the reaction. In this paper, numerical values calculated from this solvent fluctuation model and also a model in which the normal concept of activation

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** At least when $h\omega/kT \gg 1$, where ω is the frequency of vibration of ion-solvent bonds in the first solvation sheath.

by vibrational modes is taken into account are compared with experimental values of free energy of activation.

Mode of Computation

The experimental data for the standard free energy of activation ΔG^{+} (expt) for a number of homogeneous and electrochemical electron transfer reactions in solution were obtained from the experimental rate constant data by using the relation[7a] $k_r = Ze^{-\Delta G^{+}/RT}$, where the collision frequency in solution, $Z = 3 \times 10^{8}\ m^3\ mole^{-1}\ sec^{-1}$ for homogeneous[7c] and $Z = 10^{2}\ m\ sec^{-1}$ for electrochemical[7a,7b] reactions respectively.

The electrostatic continuum ΔG^{+} (continuum) and the stretching ΔG^{+} (stretch) contributions to the free energy of activation were computed by using theoretical relations from the literature given in Appendices Ia and Ib, respectively. The values of the ionic radii a_1 and a_2 were estimated from the structural geometry, radius of the corresponding metal ion and the diameter of the ligand (see tables).

Results

Data for a comparison of theory and experiment in tests of the applicability of the solvent fluctuation model to electrode reactions is sparse. However, for homogeneous reactions, —for which a similar model has been suggested[3-6],— data are plentiful.

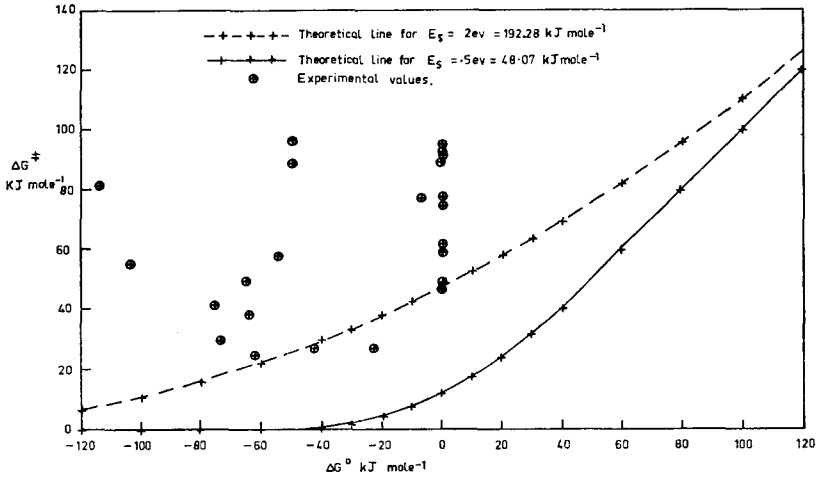

Fig. 1. Plot of free energy of activation ΔG^{+} against standard free energy of reaction ΔG^{0} for electron transfer reaction in solution from the theoretical relation of solvent fluctuation model.

TABLE 1. The calculated and the experimental free energy of activation for the non-isotopic homogeneous electron transfer reaction in solution.

Reactants	$a_1\times10^{10}$ metre	$a_2\times10^{10}$ metre	Temp °C	Standard free energy of reaction ΔG^0 kJ mole^{-1}	E_s kJ mole^{-1} (See Appendix Ia)	ΔG^* (continuum) kJ mole^{-1}	ΔG^* kJ mole^{-1}	Refs. for ΔG^* (expt)
$Fe(CN)_6^{4-}+IrCl_6^{2-}$	4.8	4.3	25	− 63.5	84.7	1.4	38.5	14
$Fe(CN)_6^{4-}+OsCl_6^{2-}$	4.8	4.2	25	− 6.7	85.8	18.4	77.3	14
$Os(dipy)_3^{2+}+IrCl_6^{2-}$	7	4.3	25	− 22.5	76.0	9.5	27.2	14
$Os(dipy)_3^{2+}+Fe(phen)_3^{3+}$	7	7	25	− 22.5	54.7	4.8	27.2	14
$Os(dipy)^{2+}+Ru^{3+}(dipy)_3$	7	7	25	− 42.2	54.7	0.7	27.2	14
$Fe^{2+}(H_2O)_6+Mn^{3+}(H_2O)_6$	3.59	3.46	25	− 53.9	108.8	6.9	58.0	15
$V^{2+}(H_2O)_6+Co(NH_3)_6^{3+}$	3.58	3.05	25	− 49.2	117.1	12.0	96.6	16
$Cr^{2+}(H_2O)_6+Fe^{3+}(H_2O)_6$	3.58	3.43	25	− 113.7	109.4	0	81.3	16
$Cr^{2+}(H_2O)_6+Co^{3+}(NH_3)_6$	3.58	3.05	25	− 49.2	117.1	12.0	89.0	16
$Fe^{2+}(H_2O)_6+Ce^{4+}(H_2O)_6$	3.59	3.77	25	− 64.6	104.3	3.8	49.4	16
$Fe^{2+}(H_2O)_6+Co^{3+}(H_2O)_6$	3.59	3.41	20	− 103.1	109.6	0.1	55.0	16
$Fe^{4-}(CN)_6+Ce^{4+}(H_2O)_6$	4.81	3.77	25	− 73.2	92.0	1.0	29.8	16
$Fe^{2+}(phen)_3+Co^{3+}(H_2O)_6$	7	3.41	25	− 75.2	93.5	0.9	41.7	16
$Mo(CN)_8^{4-}+Ce^{4+}(H_2O)_6$	4.62	3.77	25	− 61.7	93.3	2.7	24.8	16

(1) If one plots the value of $\Delta G^{\ddagger}$ calculated from the solvent fluctuation theory against the corresponding standard free energy ΔG^{0} of reaction, one obtains the result of Figure 1. The parameter, E_s used for this calculation corresponds to the range found from calculation of this parameter from the Equation (3) of Appendix Ia. It is seen that in all cases the values theoretically predicted in this model for both isotopic ($\Delta G^{0}=0$) and non-isotopic reactions are much below those observed experimentally.

Further the experimental results shown in Figure 1 from Tables 1 and 4 do not follow the trend given by the lines calculated from the solvent fluctuation model.

The lack of agreement of $\Delta G^{\ddagger}$ (continuum) and $\Delta G^{\ddagger}$ (expt) is marked also for isotopic reactions (Figs. 2 and 3, and Tables 2 and 3), for which the standard free energy of reaction is zero.

(2) The theoretical equation for $\Delta G^{\ddagger}$ (continuum) (Appendix Ia) suggests that the difference among the various couples should depend only on

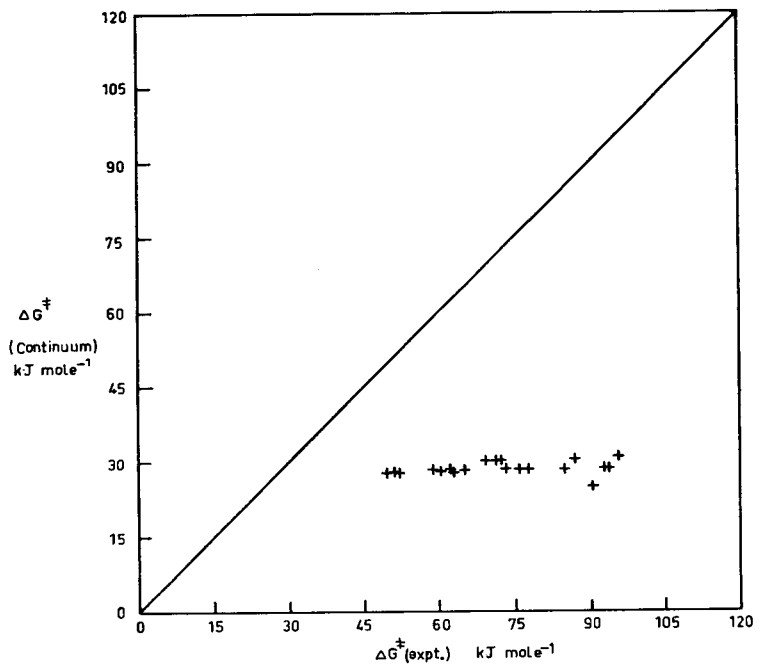

Fig. 2. Plot of $\Delta G^{\ddagger}$ (continuum) against $\Delta G^{\ddagger}$ (expt) for homogeneou electron transfer reactions in solutions involving reactants with water and ammonia molecules as ligands. (Correlation coefficient = 0.41).

TABLE 2. The calculated and the experimental free energy of activation for the homogeneous electron transfer reaction in solution.

Reactants	$a_1\times10^{10}$ metre	$a_2\times10^{10}$ metre	Temp °C	E_s kJ mole^{-1} (See Appendix Ia)	$\Delta G^{\ddagger}$ (Continuum) kJ mole^{-1}	$\Delta G^{\ddagger}$ (expt) kJ mole^{-1}	Refs. of $\Delta G^{\ddagger}$ (expt)
$Cr^{2+}(H_2O)_6$+trns $Cr^{2+}(NH_3)_5F$	3.58	3.05	25	117.1	29.3	86.3	17
$Cr^{2+}(H_2O)_6$+trns $Cr^{2+}(NH_3)_5Cl$	3.58	3.05	25	117.1	29.3	71.9	17
$Cr^{2+}(H_2O)_6$+trns $Cr^{2+}(NH_3)_5Br$	3.58	3.05	25	117.1	29.3	68.7	17
$Cr^{2+}(H_2O)_6$+trns $Cr^{2+}(NH_3)_4OH_2Cl$	3.58	3.05	25	117.1	29.3	70.8	17
$Cr^{2+}(H_2O)_6$+trns $Cr^{2+}(H_2O)_4NH_3Cl$	3.58	3.4	25	109.9	27.5	58.5	17
$Cr^{2+}(H_2O)_6+Cr^{3+}(H_2O)_5NH_3$	3.58	3.4	25	109.9	27.5	92.2	18
$Cr^{2+}(H_2O)_6$+cis$Cr^{+}(H_2O)_4Cl_2$	3.58	3.4	25	109.9	27.5	51.7	19
$Cr^{2+}(H_2O)_6$+trns $Cr^{+}(H_2O)_4Cl_2$	3.58	3.4	25	109.9	27.5	50.9	19
$Cr^{2+}(H_2O)_6+Cr^{2+}(H_2O)_5H_2PO_2$	3.58	3.4	25	109.9	27.5	84.3	20
$Tl^{+}(H_2O)_6+Tl^{3+}(H_2O)_6$	4.25	3.81	25	95.7	23.9	89.6	21
$Cr^{2+}(H_2O)_6+Cr^{2+}(H_2O)_5CN$	3.56	3.4	25	110.2	27.5	72.8	22
$Ru^{2+}(NH_3)_6+Ru^{3+}(NH_3)_6$	3.57	3.47	25	108.8	27.2	49.1	23
$Co^{2+}(NH_3)_6+Co^{3+}(NH_3)_6$	3.59	3.05	64.5	119.4	29.8	94.9	24
$Co^{2+}(H_2O)_6+Co^{3+}(H_2O)_6$	3.56	3.41	25	110.0	27.5	61.8	25
$Cr^{2+}(H_2O)_6+Cr^{2+}(H_2O)_5F$	3.56	3.41	25	110.0	27.5	75.3	26
$V^{2+}(H_2O)_6+V^{3+}(H_2O)_6$	3.58	3.385	24.8	110.2	27.5	64.4	27
$Fe^{2+}(H_2O)_6+Fe^{3+}(H_2O)_6$	3.59	3.43	0	109.3	27.3	59.9	28
$Cr^{2+}(H_2O)_6+Cr^{3+}(H_2O)_6$	3.58	3.4	25	109.9	27.5	92.8	29
$Mn^{2+}(H_2O)_6+Mn^{3+}(H_2O)_6$	3.66	3.46	25	107.8	26.9	62.4	30
$V^{2+}(H_2O)_6+V^{3+}(H_2O)_6$	3.58	3.385	25	110.2	27.5	77.3	31

TABLE 3. The calculated and the experimental free energy of activation for homogeneous electron transfer reaction in solution having reactants with big organic ligands.

Reactants	$a_1\times10^{10}$ metre	$a_2\times10^{10}$ metre	Temp °C	E_s kJ mole^{-1} (See Appendix Ia)	ΔG^* (continuum) kJ mole^{-1}	ΔG^* (expt) kJ mole^{-1}	Refs. of ΔG^* (expt)
$Fe(CN)_6^{4-}+Fe(CN)_6^{3-}$	4.81	4.65	39	81.0	20.3	48.9	32
$Fe(CN)_6^{4-}+Fe(CN)_5^{2-}NH_3$	4.81	4.65	25	81.0	20.3	43.8	33
$Fe(CN)_6^{4-}+Fe(CN)_5^{2-}H_2O$	4.81	4.65	25	81.0	20.3	48.6	33
$Co(EDTA)^{2-}+Co(EDTA)^-$	2.93	3.03	25	128.9	32.2	102.5	34
$Co(EDTA)^-+Co(EDTA)^-$	2.93	3.03	100	128.9	32.2	108.9	35
$Fe^{2+}(H_2O)_6+Fe(C_2O_4)_3^{3-}$	3.59	2.67	20	131.5	32.9	45.9	36
$Co(phen)_3^{2+}+Co(phen)_3^{3+}$	6.85	6.76	0	56.6	14.2	60.1	37
$Co^{2+}(en)_3+Co^2(en)_3^{3+}$	3.14	3.04	50	124.0	31.0	95.3	38
$Co^{2+}(en)_3+Co^{2+}(en)_3OH$	3.14	3.04	50	124.0	31.0	90.0	38
$Co^{2+}(en)_3+Co^{2+}(en)_3Cl$	3.14	3.04	50	124.0	31.0	91.9	38
$Co^{2+}(en)_3+Co^{+}(en)_3SO_4$	3.14	3.04	50	124.0	31.0	95.5	38
$Fe^{2+}(H_2O)_6+Fe^{3+}(phen)_3$	3.54	7	25	89.4	22.3	39.2	39

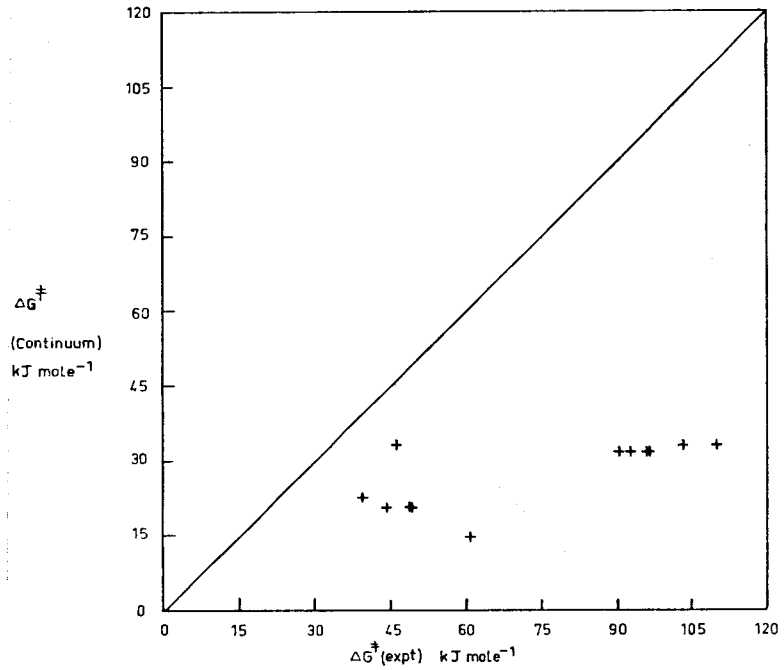

Fig. 3. Plot of $\Delta G^{\ddagger}$ (oontinuum) against $\Delta G^{\ddagger}$ (expt) for homogeneous electron transfer reactions in solution involving reactants with big organic ligands. (Correlation coefficient = 0.4).

the radius. Experimentally, the variation of $\Delta G^{\ddagger}$ (expt) among the 47 examples chosen is much *greater* than that of the theory (Figs. 2, 3 and 8).

(3) For ions large enough to have no primary solvation sheath[8] attached to them, a continuum theory might be expected to work better. The calculated values of $\Delta G^{\ddagger}$ (continuum) show no better agreement with the experimental free energy of activation for the reaction involving large ions (with big organic ligands), than for ions with small ligands (Fig. 3 and Table 3).

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* The extent of correlation can be found from a correlation coefficient which gives a measure of how close the data points are to the line of unit slope. The value of 1 of correlation coefficient corresponds to all data points on the line of unit slope and thus represents 100% correlation between calculated and experimental values.

$$\text{Correlation Coefficient} = 1 - \sum \frac{(x-y)}{L} / n$$

where $L = \begin{matrix} x \text{ for } x > y \\ y \text{ for } x < y \end{matrix}$

and n = number of data points

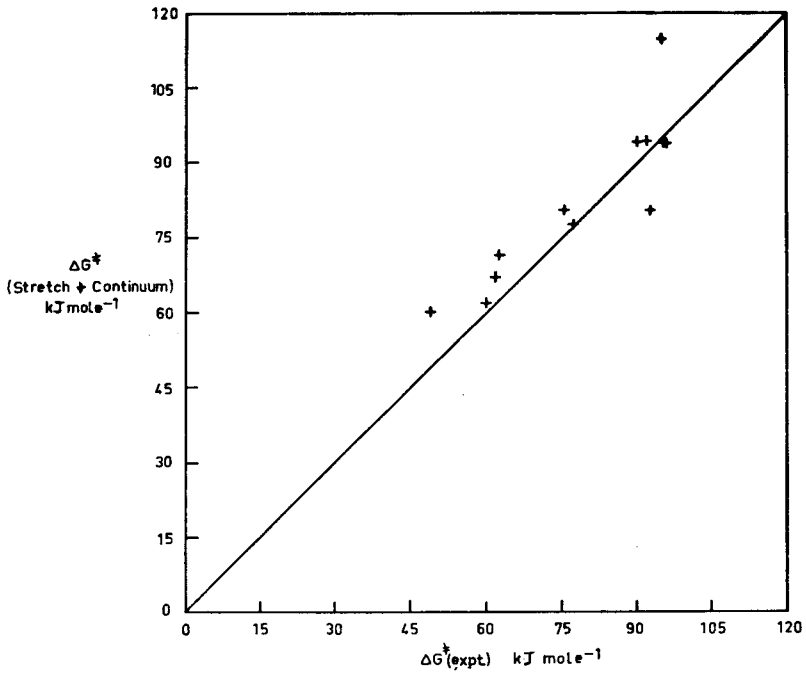

Fig. 4. Plot of ΔG^* (continuum+stretch) against ΔG^* (expt) for homogeneous electron transfer reactions in solution. (Correlation coefficient = 0.93).

(4) Agreement between theoretical and experimental free energy of activation is observed if the stretching contribution (Appendix Ib) of the inner co-ordinated bond is added to the continuum electrostatic contribution (Fig. 4 and Table 4). Fair correlation* is observed between theory and experiment for both homogeneous and electrochemical cases if the *electrostatic contribution is entirely neglected,* and only the stretching contribution considered (Figs. 5 and 6, and Tables 4 and 6). For the electrochemical redox reactions, better agreement is observed when both stretching and electrostatic contributions are used (Fig. 7, Tables 5 and 6), *but an estimation based solely on the continuum theory gives no agreement with experiment* (Fig. 8, Table 6). The experimental data needed to calculate the stretching contribution for both homogeneous and electrochemical reactions are given in Table 7.

(5) According to the solvent fluctuation estimate, one expects a low value of the reorganization energy of large ions such as Co^{+3} $(phen)_3$,

* See the footnote on page 7

TABLE 4. Calculated values for both continuum and stretching contribution to the free energy of activation for the homogeneous electron transfer reaction in solution.

Reactants	Temp °C	$\Delta G^{\neq}$ (continuum) kJ mole^{-1}	$\Delta G^{\neq}$ (stretch) kJ mole^{-1}	$\Delta G^{\neq}$ (continuum + stretch) kJ mole^{-1}	$\Delta G^{\neq}$ (expt) kJ mole^{-1}
$Co^{2-}(H_2O)_6+Co^{3+}(H_2O)_6$	25	27.5	39.4	66.9	61.8
$V^{2+}(H_2O)_6+V^{3+}(H_2O)_6$	0	27.5	50.0	77.5	77.3
$Fe^{2+}(H_2O)_6+Fe^{3+}(H_2O)_6$	25	27.3	34.5	61.8	59.9
$Cr^{2+}(H_2O)_6+Cr^{3+}(H_2O)_6$	25	27.5	52.9	80.4	92.8
$Co^{2+}(en)_3+Co^{3+}(en)_3$	50	31.0	63.0	94.0	95.3
$Co^{2+}(en)_3+Co^{2+}(en)_3OH$	50	31.0	63.0	94.0	90.0
$Mn^{2+}(H_2O)_6+Mn^{3+}(H_2O)_6$	25	26.9	44.2	71.1	62.4
$Cr^{2+}(H_2O)_6+Cr^{2+}(H_2O)_6F$	25	27.5	52.9	80.4	75.3
$Co^{2+}(en)_3+Co^{2+}(en)_3Cl$	50	31.0	63.0	94.0	91.9
$Fe^{3-}(CN)_6+Fe^{4-}(CN)_6$	25	20.3	39.8	60.1	48.9
$Co^{2+}(en)_3+Co^{+}(en)_3SO_4$	50	31.0	63.0	94.0	95.5
$Co^{2+}(NH_3)_6+Co^{3+}(NH_3)_6$	25	29.9	84.6	114.4	94.9

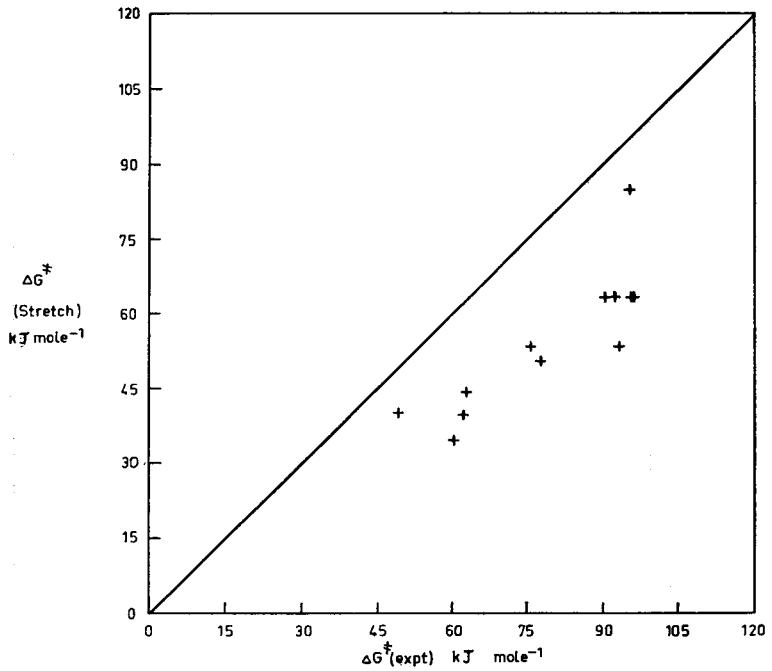

Fig. 5. Plot of $\Delta G^{\ddagger}$ (stretch) against $\Delta G^{\ddagger}$ (expt) for homogeneous electron transfer reactions in solutions. (Correlation coefficient = 0.7).

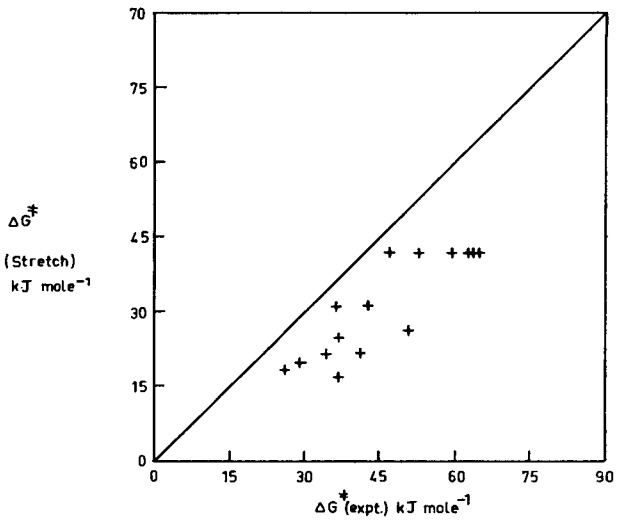

Fig. 6. Plot of $\Delta G^{\ddagger}$ (stretch) against $\Delta G^{\ddagger}$ (expt) for the *electrochemical* electron transfer reactions. (Correlation coefficient = 0.7).

TABLE 5. Experimental data of standard free energy of activation of *electrochemical* electron transfer reactions in solution used for comparison with the theoretical values.

Systems	Temp °C	Electrode	Medium	$\Delta G^{\ddagger}$ (expt) kJ mole^{-1}	Refs.
$Ce^{4+}(H_2O)_6$	25	Pt	$1MH_2SO_4$	42.6	40
$Cr^{3+}(H_2O)_6$	20	Hg	1MKCl	50.7	41
$Co(NH_3)_6^{3+}$	25	Hg		52.7	42
$[Co(NH_3)_5NO_2]^{2+}$	25	Dropping Hg-electrode (DME)	$0.14MHClO_4$ $+1.26M$ $NaClO_4$	63.5	43
$[Co(NH_3)_5(ONO)]^{2+}$	25	DME	"	62.7	43
cis-$[Co(NH_3)_4(NO_2)_2]^{+}$	25	DME	"	59.3	43
trans-$[Co(NH_3)_4(NO_2)_2]^{+}$	25	DME	"	64.7	43
$Cr(CN)_6^{3-}$	20	Hg	1MKCN	25.9	41
$Co(en)_3^{2+}$	25	Pt	2NKCl	36.0	44
$Fe^{2+}(H_2O)_6$	25	Pt-rotating disc electrode	$1MH_2SO_4$	36.5	40
$Fe(CN)_6^{3-}$	25	Pt	1MKCl	28.9	40
$V^{3+}(H_2O)_6$	20	Hg	$1MHClO_4$	36.6	45
$Ti^{4+}(H_2O)_6$	20	Hg	1M-tertric	34.4	41
$[Co(NH_3)_5F]^{2+}$	25	DME	$0.14MHClO_4$ $+1.26M$ $NaClO_4$	46.8	43
$Mn(H_2O)_6^{2+}$	22	Pt	$4MHClO_4$	41.0	9

TABLE 6. Calculated values for both continuum and stretching contribution to the experimental free energy of activation for the electrochemical redox reaction.

Systems	$a_1 \times 10^{10}$ metre	E_s kJ mole^{-1}	$\Delta G^{\neq}$ (continuum) kJ mole^{-1}	$\Delta G^{\neq}$ (stretch) kJ mole^{-1}	$\Delta G^{\neq}$ (continuum +stretch)	$\Delta G^{\neq}$ (expt) kJ mole^{-1}
$Ce^{4+}(H_2O)_6$	3.77	50.8	12.7	31.6	44.3	42.6
$Cr^{3+}(H_2O)_6$	3.4	56.4	14.1	26.4	40.5	50.7
$Co^{3+}(NH_3)_6$	3.05	62.7	15.7	42.3	58.0	52.7
$[Co(NH_3)_5NO_2]^{2+}$	3.05	62.7	15.7	42.3	58.0	63.5
$V^{3+}(H_2O)_6$	3.385	56.5	14.1	25.0	39.1	36.6
$Ti^{4+}(H_2O)_6$	3.52	54.3	13.5	21.8	35.3	34.1
cis-$[Co(NH_3)_4(NO_2)_2]^{+}$	3.05	62.7	15.7	42.3	58.0	59.3
Trans-$[Co(NH_3)_4(NO_2)_2]^{+}$	3.05	62.7	15.7	42.3	58.0	64.8
$Cr(CN)_6^{3-}$	4.63	41.3	10.3	18.8	29.1	25.9
$[Co(NH_3)_5F]^{2+}$	3.05	62.7	15.7	42.3	58.0	46.8
$Co(en)_3^{3+}$	3.04	63.0	15.7	31.3	47.0	36.0
$[CO\text{-}(NH_3)_5ONO]^{2+}$	3.05	62.7	15.7	42.3	58.0	62.7
$Fe^{3+}(H_2O)_6$	3.43	55.8	13.9	17.2	31.1	36.5
$Mn^{3+}(H_2O)_6$	3.46	55.3	13.8	22.1	35.9	41.0
$Fe(CN)_6^{3-}$	4.65	40.4	10.1	19.9	30.0	28.9

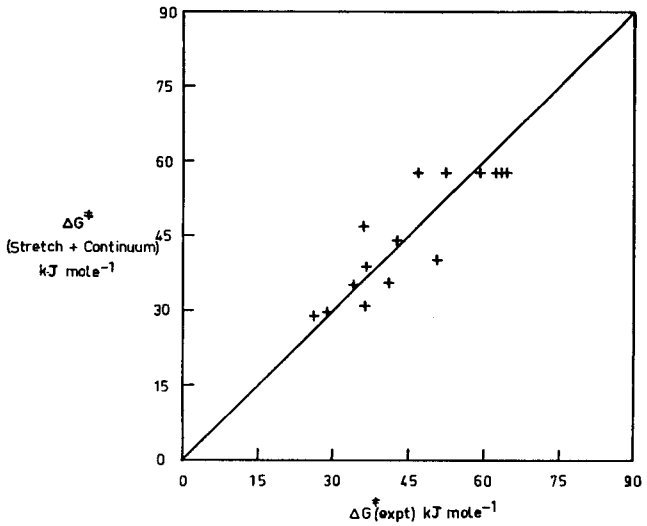

Fig. 7. Plot of $\Delta G^{\ddagger}$ (continum + stretch) against $\Delta G^{\ddagger}$ (expt) for *electrochemical* electron transfer reactions. (Correlation coefficient = 0.9).

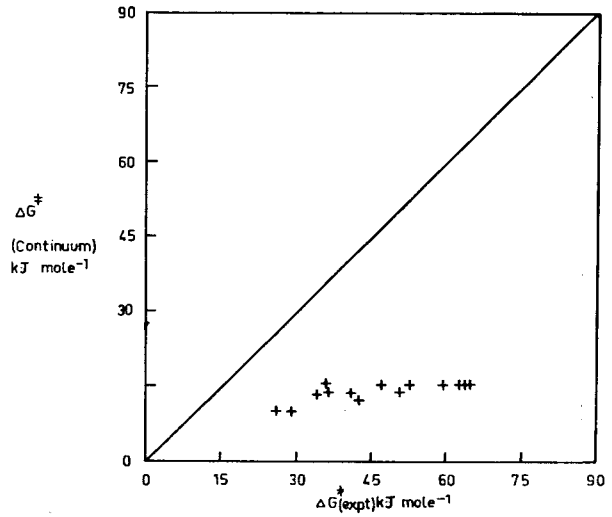

Fig. 8. Plot of $\Delta G^{\ddagger}$ (continuum) against $\Delta G^{\ddagger}$ (expt) for *electrochemical* electron transfer reactions. (Correlation coefficient = 0.33).

TABLE 7. Experimental data required for calculation of stretching contribution to standard free energy of activation for electron transfer reactions in solution* (For definition of symbols see Appendix Ib and Ic)

Systems	Stretching frequency $\bar{\nu}_0$ cm^{-1}	Stretching frequency $\bar{\nu}_r$ cm^{-1}	f_0 m dyne/Å (calc)	f_r m dyne/Å (calc)	Δq $\times 10^{10}$ metre	References for Δq	References for $\bar{\nu}_0$ and $\bar{\nu}_r$
$Fe^{3+}(H_2O)_6+Fe^{2+}(H_2O)_6$	490	389	1.93	1.22	0.16	46	51
$Co^{3+}(H_2O)_6+Co^{2+}(H_2O)_6$	490	389	1.95	1.22	0.17	46	51
$Cr^{3+}(H_2O)_6+Cr^{2+}(H_2O)_6$	490	389	1.89	1.19	0.18	47	51
$Mn^{3+}(H_2O)_6+Mn^{2+}(H_2O)_6$	490	395	1.92	1.25	0.2	47	51
$V^{3+}(H_2O)_6+V^{2+}(H_2O)_6$	490	389	1.89	1.19	0.195	46.48	51
$Ce^{4+}(H_2O)_6+Ce^{3+}(H_2O)_6$	550	490	2.74	2.17	0.17	46	51
$Fe(CN)_6^{3-}+Fe(CN)_6^{4-}$	511	585	1.52	1.99	0.16	46	51.55
$Co^{3+}(NH_3)_6+Co^{2+}(NH_3)_6$	328	318	0.84	0.78	0.34	49	52
$Co^{3+}(en)_3+Co^{2+}(en)_3$	585	502	2.54	1.87	0.18	50	53
$Co^{3+}(en)_3+Co^{+}(en)_3OH$	585	502	2.54	1.87	0.18	50	53
$Co^{2+}(en)_3+Co^{2+}(en)_3Cl$	585	502	2.54	1.87	0.18	50	54
$Co^{2+}(en)_3+Co^{+}(en)_3SO_4$	585	502	2.54	1.87	0.18	50	54
$Co^{2+}(en)_3+Co^{2+}(en)_3Br$	585	502	2.54	1.87	0.18	50	54
$Co^{2+}(en)_3+Co^{2+}(en)_3I$	585	502	2.54	1.87	0.18	50	54
$[Co(NH_3)_5NO_2]^{3+}+[Co(NH_3)_5NO_2]^{+}$	328	318	1.85	1.3	0.34	49	52
$[Co(NH_3)_5ONO]^{2+}+[Co(NH_3)_5ONO]^{+}$	328	318	1.85	1.3	0.34	49	52
cis-$[Co(NH_3)_4(NO_3)_2]^{+}$ + cis-$[Co(NH_3)_4(NO_2)_2]$	328	318	2.03	1.43	0.34	49	52
trans-$[Co(NH_3)_4(NO_2)_2]^{+}$ + trans-$[Co(NH_3)_4(NO_2)_2]$	328	318	1.97	1.37	0.34	49	52
$Cr(CN)_6^{3-}+Cr(CN)_6^{4-}$	511	585	1.51	2.42	0.16	46	56
$[Co(NH_3)_5F]^{2+}+[Co(NH_3)+F]$	485	407	1.83	1.25	0.34	49	52

* Some values were estimated on the basis of an analogy with ions of similar structure.

$Co(EDTA)^-$, $Co^{+3}(en)_3$, *etc* (15–30 $kJ\,mole^{-1}$). Experimentally, fairly *high* values, 39 to 108 $kJ\,mole^{-1}$, are observed (Table 3). Contribution to the free energy of activation evidently comes mainly from the stretching of the co-ordinated bond of the complex (Figs. 4 and 7).

(6) In the types of redox couples we used, the difference in the ions of high and low valence states is only in the bond lengths in the two states, the geometry and number of co-ordinated groups are the same. The change in the co-ordinated bond lengths in the two states is not consistent with the solvent fluctuation model of redox reactions, according to which the bond length of ion ligand bond in the two valence state of the redox couples should be the same.

(7) Calculations[9] in which a higher fraction has been claimed for the electrostatic contribution were achieved by taking out of Equation (2) of Appendix Ia the image term, $\frac{(ne_0)^2}{2r}\left(\frac{1}{D_{op}}-\frac{1}{D_S}\right)$. This approximately *doubles* the value of the ΔG^* (continuum)[7b] and makes it identical for homogeneous and heterogeneous cases. However, other authors[10-12] support the contribution of image effect near surfaces.

Thus (Tables 8 and 9), the reorganization contribution to the free energy

TABLE 8. The percentage contribution of ΔG^* (stretch) and ΔG^* (continuum) to the ΔG^* (continuum+stretch) for the homogeneous electron transfer reaction in solution.

Systems	Temp °C	% contribution of ΔG^* (stretch) to ΔG^* (continuum +stretch)	% contribution of ΔG^* (continuum) to ΔG^* (continuum +stretch)
$Co^{2+}(H_2O)_6+Co^{3+}(H_2O)_6$	64.5	58.9	41.1
$V^{2+}(H_2O)_6+V^{3+}(H_2O)_6$	25	64.5	35.5
$Fe^{2+}(H_2O)_6+Fe^{3+}(H_2O)_6$	25	55.8	44.2
$Cr^{2+}(H_2O)_6+Cr^{3+}(H_2O)_6$	25	65.8	34.2
$Co^{2+}(en)_3+Co^{3+}(en)_3$	25	67.0	33.0
$Co^{2+}(en)_3+Co^{2+}(en)_3OH$	25	67.0	33.0
$Mn^{2+}(H_2O)_6+Mn^{3+}(H_2O)_6$	25	62.1	37.8
$Cr^{2+}(H_2O)_6+Cr^{2+}(H_2O)_6F$	50	65.8	34.2
$Co^{2+}(en)_3+Co^{2+}(en)_3Cl$	50	67.0	33.0
$Fe^{3-}(CN)_6+Fe^{4-}(CN)_6$	50	66.2	33.7
$Co^{2+}(en)_3+Co^{+}(en)_3SO_4$	25	67.0	33.0
$Co^{2+}(NH_3)_6+Co^{3+}(NH_3)_6$	50	73.7	26.3

TABLE 9. The percentage contribution of ΔG^{+} (stretch) and ΔG^{+} (continuum) to the ΔG^{+} (stretch+ continuum) for the electrochemical electron transfer reaction.

Reactants	Temp °C	% contribution of ΔG^{+} (stretch) to ΔG^{+} (continuum +strecth)	% contribution of ΔG^{+} (continuum) to ΔG^{+} (continuum +stretch)
$Ce^{4+}(H_2O)_6$	25	71.3	28.7
$Cr^{3+}(H_2O)_6$	20	65.2	34.8
$Co^{3+}(N_3H)_6$	25	72.9	27.1
$[Co(NH_3)_5NO_2]^{2+}$	25	72.9	27.1
$V^{3+}(H_2O)_6$	20	63.9	36.1
$Ti^{4+}(H_2O)_6$	20	61.6	38.4
cis-$[Co(NH_3)_4(NO_2)_2]^{+}$	25	72.9	27.1
trans-$[Co(NH_3)_4(NO_2)_2]^{+}$	25	72.9	27.1
$Cr(CN)_6^{3-}$	20	64.5	35.5
$[Co(NH_3)_5F]^{2+}$	25	72.9	27.1
$Co(en)_3^{3+}$	25	66.6	33.4
$[Co(NH_3)_5ONO]^{2+}$	25	72.9	27.1
$Fe(H_2O)_6^{3+}$	25	55.2	44.8
$Mn^{3+}(H_2O)_6$	22	61.5	38.5
$Fe(CN)_6^{3-}$	25	66.6	33.4

of activation is only about one-third of the total value in redox processes in aqueous solution.

Discussion

The present comparisons show that about two-thirds of the free energy of activation in redox reactions in solution comes from *bond stretching* for both homogeneous and electrochemical electron transfer reactions. Thus, the activation of the vibrational modes is the more significant mode of activation. In an earlier paper[9], taking eight electrochemical redox systems of inorganic complex, a greater contribution from continuum theory was claimed. To obtain this result, the electrostatic continuum value of the free energy of activation for electrochemical reactions was calculated by *neglecting the image term* and by using UREY-BRADLEY force constants (UBFC) for the inorganic redox couple.

In selecting appropriate force constants for the symmetrical stretching frequencies, we have taken experimental values (Appendix Ic and Table 7).

In particular, one should *not* take UREY-BRADLEY force constants, because here the total energy acting on the bond from the stretching of the bond itself, and the interactions with the bond of non-bonding atoms, are resolved into two force constants, one of which is then taken out as the "stretching" force constants*. This constant has been used earlier[9] in the calculation of stretching energies. However, one should use the *net* stretching force constant, caused by all interactions of the bond concerned with other bonds as the parameter upon which the stretching energy is based. Hence, experimental values of stretching force constants are the relevant ones.

The above remarks show why it was earlier[9] concluded that there was a greater contribution from the continuum solvent fluctuation than we here conclude. Had the experimental stretching force constants and the image energy term been used, then results similar to ours would have been obtained.

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Appendix I

(a) The following theoretical relations were used for the estimation of free energy of activation $\Delta G^{\ddagger}_{0\,\mathrm{calc}}$ from the continuum solvent fluctuation model[6]

$$\Delta G^{\ddagger}\,(\text{continuum}) = \begin{cases} \Delta G^0 & \text{for } E_s \leqslant \Delta G^0 \\ \dfrac{(E_s + \Delta G^0)}{4E_s} & \text{for } -E_s < \Delta G^0 < E_s \\ 0 & \text{for } E_s \leqslant -\Delta G^0 \\ \dfrac{E_s}{4} & \text{for } \Delta G^0 = 0 \end{cases} \qquad (1)$$

where ΔG^0 = standard free energy of the reaction

E_s = free energy of re-organisation (see Fig. 9)

* There is an error in sign in the originalUREY-BRADLEY paper[12a], where the non-bonding atoms are taken to interact attractively with the bonded one, whereas the interaction would usually be repulsive. Had this reversal been taken into account, the force constant from the UREY-BRADLEY calculations would have been greater than the experimental one we would have used, and would have given an even larger value of the stretching contribution to the free energy of activation than we obtained using experimental stretching force constants.

$$= \frac{(ne_0)^2}{2}\left(\frac{1}{a_1}-\frac{1}{r}\right)\left(\frac{1}{D_{op}}-\frac{1}{D_s}\right) \text{ for electrochemical reaction,} \quad (2)$$

and $$E_s = (ne_0)^2\left(\frac{1}{2a_1}+\frac{1}{2a_2}-\frac{1}{r}\right)\left(\frac{1}{D_{op}}-\frac{1}{D_s}\right) \text{ for homogeneous reaction,} \quad (3)$$

where a_1 and a_2 are the radii of the reacting ions with their inner solvation sheath, r is double the distance from the centre of the ion to the electrode surface for electrochemical reactions, and $r=(a_1+a_2)$ in homogeneous reactions. n is the number of electrons transferred during reaction and

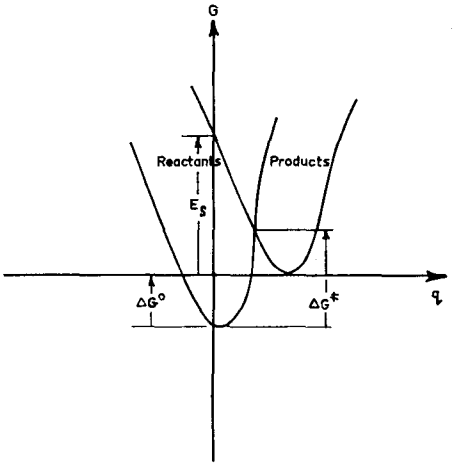

Fig. 9. Free energy curves showing the relation between E_s, $\Delta G^{\neq}$ and ΔG^0.

e_0 is the electronic charge. D_{op} and D_s are the optical and static dielectric contant of the medium.

(b) For the estimation of the stretching contribution to the free energy of activation $\Delta G^{\neq}$ (stretch) the following relation[13] has been used

$$\Delta G^{\neq}(\text{stretch}) = \frac{m f_r f_0}{2(f_r+f_0)}(\Delta q)^2 \quad (4)$$

where f_r = force constant of the metal ligand co-ordinated bond of reduced ion,

f_0 = force constant of the metal ligand co-ordinated bond of oxidised ion,

Δq = the equilibrium metal-ligand bond length difference of oxidised

and reduced species,

m = number of ligands co-ordinated with metal ion.

For electrochemical electron transfer reaction:

$$\Delta G^{*}(\text{stretch}) = \frac{1}{2}\left(\frac{m f_r f_0}{2(f_r+f_0)}(\Delta q)^2\right). \tag{5}$$

(c) $$\bar{\nu}_0 = \frac{1}{2\pi c}\sqrt{f_0/\mu} \tag{6}$$

and $$\bar{\nu}_r = \frac{1}{2\pi c}\sqrt{f_r/\mu} \tag{7}$$

when $\bar{\nu}_0$ = experimental stretching frequency in cm^{-1} for oxidised state,

$\bar{\nu}_r$ = experimental stretching frequency in cm^{-1} for reduced state,

f_0 = force constant for oxidised state,

f_r = force constant for reduced state,

c = velocity of light,

μ = reduced mass.

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