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Free Energies of Hydration for Metal Ions from Heats of Vaporization

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Abstract

Consistent thermochemical data are of major importance for predicting and rationalizing stability and reactivity throughout chemistry. The free energy of hydration (ΔG_{hyd}) substantially defines the aqueous chemistry of metal ions and aids our understanding of the properties of water and has thus been widely studied both theoretically and experimentally. This paper first shows that the experimental standard half reduction potential for the process $M^{n+} + n e^- \rightarrow M$ is accurately described using a simplified version of Trasatti's thermochemical cycle involving the ionization potentials, ΔG_{hyd} of M^{n+} , and the standard heat of vaporization (ΔH_{vap}) of M . This approximation, which neglects entropy, is shown to be valid both by actual performance (uncertainty ~ 0.1 V, $R^2 \sim 0.99$ -1.00 for available data for M^{3+} and M^{2+} ions) and by application of Trouton's rule for entropies of vaporization. Second, application of the formula allows the identification of many ΔG_{hyd} values not reported before. Together with previously determined values, the compiled lists of ΔG_{hyd} are the most complete so far reported and are all thermochemically consistent, i.e. they agree with their corresponding thermochemical cycles. The numbers use the convention $\Delta G_{\text{hyd}}(\text{H}^+) = -1100$ kJ/mol and SHE = +4.44 V, but can be easily adjusted to other reference states as appropriate. Some of the new ΔG_{hyd} values established here are for the catalytically important d-transition metal ions Rh^{3+} , Re^{3+} , Ir^{3+} , Mo^{3+} , W^{3+} , Ge^{2+} , Tc^{2+} , Nb^{3+} , Ta^{3+} , Os^{3+} , and Ru^{2+} . Some, such as Ir^{3+} , are among the most inert aqua ions known. The ΔG_{hyd} values have an accuracy of ~ 10 kJ/mol and are recommended for use in thermochemical calculations, for interpretation of the aqueous chemistry of the metal ions, and as benchmarks for theoretical chemistry.

Introduction

The behavior of metal ions (M^{n+}) in water is of central importance to a wide range of processes in biology and chemistry and tells us much about the unique properties of water as a solvent.^{1–6} Specifically, the hydration free energy $\Delta G_{\text{hyd}}(M^{n+})$ greatly contributes to the chemistry of the metal ion in aqueous solution and determines the ability of a metal ion to associate with or dissociate from water e.g. during transport through membranes or binding to host molecules.^{3,7–9} The relative magnitude of $\Delta G_{\text{hyd}}(M^{n+})$ determines much of the selectivity of different ions toward host molecules such as proteins, membranes, and other macromolecules and materials.^{10–13} The $\Delta G_{\text{hyd}}(M^{n+})$ is also important for understanding the redox chemistry and stability of ions in solution, as $\Delta G_{\text{hyd}}(M^{n+})$ directly relates the vacuum ionization potential to the standard reduction potential of M .^{14–18}

Values of $\Delta G_{\text{hyd}}(M^{n+})$ derived from experiment constitute important benchmark data for understanding these phenomena and for the evaluation of theoretical methods such as semi-classical water models, density functional theory (DFT), and classical force fields.^{19–26} The simulated properties of an ion in water studied by molecular dynamics depends critically on the $\Delta G_{\text{hyd}}(M^{n+})$ that the applied force field produces, as any error in this value biases the tendency of the ion to stick within its current hydration shell, and these energies should be put on scale with corresponding anions to avoid artefacts in water's preferential association with the ions.^{27,28} When simulating ion-host systems such as channels and ion pumps one should use classical force fields that adequately describe $\Delta G_{\text{hyd}}(M^{n+})$ by explicit parameterization to experimental values, to enable an accurate description of the energetics of moving the ion from water to the host.

Many values of $\Delta G_{\text{hyd}}(M^{n+})$ have been tabulated by e.g. Noyes²⁹, Rosseinsky³⁰, Fawcett³¹, Rizkalla and Choppin³², and Latimer^{16,17}, and in particular by Marcus^{8,33,34}. It is important to create a consensus among these values. It is also important to ensure that these values are “thermochemically consistent”, i.e. that they are consistent with other data when applied in thermochemical cycles.³⁵ Following the work of Trasatti, one can calculate $\Delta G_{\text{hyd}}(M^{n+})$ from thermochemical cycles involving the standard half potentials $E_{1/2}^0$ and ionization potentials (IP).^{14,36,37} Emphasis should be on adhering to acceptable standard states (298.15 K; unity activity; 1 atm partial pressure) and consensus reference values of $\Delta G_{\text{hyd}}(H^+) = -1100 \pm 3 \text{ kJ/mol}$ ^{38,39} and the standard hydrogen electrode (SHE), $E_{\text{SHE}}^0(\text{abs}) = +4.44 \text{ V} \pm 0.02 \text{ V}$ ³⁷.

Using this principle, new consistent $\Delta G_{\text{hyd}}(M^{n+})$ values for all divalent and trivalent metal ions M^{2+} and M^{3+} were recently calculated by using the gas phase ionization potentials, which are available at very high accuracy, and the many tabulated values of standard reduction potentials.³⁵ Since these data

rely on those of Marcus in at least one of the oxidation states they also rely on the tetraphenylarsonium tetraphenylborate (TATB) extra-thermodynamic assumption for separating anion and cation hydration⁴⁰ and carry the same potential flaws^{41,42}; however comparison to available data once corrected for reference states indicates errors of the order of ~ 10 kJ/mol, which is close to the limit of accuracy achievable for the absolute potentials.^{35,37} This protocol requires a thermochemical cycle of M^{3+} and M^{2+} ions together, thus obscuring values for many important metal ions. For example, the free energy of hydration of catalytically important ions such as Rh^{3+} , Re^{3+} , Ir^{3+} , W^{3+} , and Ru^{2+} are not tabulated in the references mentioned above and would be valuable assets to the thermochemically consistent scale.

In the present paper, it is shown that values of $\Delta G_{hyd}(M^{n+})$ can be obtained from a thermochemical cycle using the heat of vaporization as a proxy of the atomization free energy of the metal, as the introduced entropy error is small. Since many values of heats of vaporization are known at good accuracy for metals⁴³, this enables the computation of several new $\Delta G_{hyd}(M^{2+})$ and $\Delta G_{hyd}(M^{3+})$ values. Since these values are derived from experimental data only, they have the same accuracy as the involved experiments, or as shown here having a numerical accuracy of ~ 10 kJ/mol and a trend accuracy of $R^2 = 0.99-1.00$. New ΔG_{hyd} values are established for important d-transition metal ions Rh^{3+} , Re^{3+} , Ir^{3+} , Mo^{3+} , W^{3+} , Ge^{2+} , Tc^{2+} , Nb^{3+} , Ta^{3+} , Os^{3+} , and Ru^{2+} .

Figure 1. Thermochemical cycle used to calculate standard half reduction potential of the metal M. The dashed rectangle describes the cycle approximated in this work, whereas the remaining steps to the right represent important processes from a measuring perspective, which include the work functions of the metal M; (m), (g), and (aq) refer to the pure metal, gas, and aqueous states, respectively. Please see text for further details.

Methods

Conventions used. The values reported in this paper refer to the standard states applied in the experimental data from which they were derived, i.e. unity activities (~ 1 M concentrations), $T = 298.15$ K, and 1 atm pressure. The values are reported relative to the value of the hydration free energy of the proton, $\Delta G_{hyd}(H^+)$. In previous work³⁵ as well as here, we use the modern consensus of $\Delta G_{hyd}(H^+) = -1100 \pm 5$ kJ/mol, based mainly on the values by Zhan and Dixon (-1098 kJ/mol)⁴⁴ and Tissandier et al. (-1104.5 kJ/mol).³⁸ $\Delta G_{hyd}(H^+)$ differs from the chemical potential of the proton in water, $\mu(H^+)(aq)$ by the value of the surface potential of water, χ^S as described by Equation (1):^{37,45}

$$\Delta G_{hyd}(H^+) = \mu(H^+)(aq) - F\chi^S \quad (1)$$

where F is Faraday's constant converting from potential to energy. The standard chemical potential of the proton was calculated by Trasatti³⁷ and Farrell and McTigue⁴⁶ to be -1088 kJ/mol. Fawcett⁴⁵ obtained this value from the work function of mercury and another value of -1091 kJ/mol by analyzing the data reported by Randles⁴⁷. This gives an estimate of the accuracy of this number of ± 3 kJ/mol. From the difference according to Equation (1) the surface potential χ^S was estimated by Trasatti to be $+0.13$ V³⁷, by Farrell and McTigue to be $+0.025$ V⁴⁶, and by Krishtalik to be $+0.14$ V⁴⁸. In addition, Parfenyuk has estimated a consensus value of $+0.10$ V from a survey of data⁴⁹. Thus, χ^S has an accuracy of ± 0.05 V (5 kJ/mol). These points were discussed by Farrell and McTigue, who computed the numbers

as +4.31 V and +4.44 V⁴⁶; the latter is the value of SHE used here. Considering the experimental measurement uncertainties of perhaps ~5 kJ/mol, the values of $\Delta G_{\text{hyd}}(\text{M}^{n+})$ reported in this work has an estimated uncertainty of ± 10 kJ/mol as confirmed by explicit calculation below. The uncertainty is probably slightly larger for the trivalent ions, since we can expect that the errors scale monotonously with the magnitude of ΔG_{hyd} .

Thermochemical cycle and heat approximation. The thermochemical cycle used in this work is shown in **Figure 1** and follows closely the work by Trasatti.³⁷ The work functions corresponding to the bulk and vacuum situations are included for completeness but not used in this work (the work function is included in the metal-solvent bulk potential difference, written $\Delta\Phi$ in **Figure 1**). For the purpose of the present work, the standard half reduction potential $E_{1/2}^0(\text{M}^{n+}/\text{M})$ for a metal M,

can be computed from a Born-Haber cycle³⁷:

$$E_{1/2}^0(\text{M}^{n+}/\text{M}) = (\Delta G_{\text{at}}^0 + \Delta G_{\text{IP}}(\text{M}) + \Delta G_{\text{hyd}}(\text{M}^{n+}))/nF - \text{SHE} \quad (3)$$

which is reflected by the dashed rectangle in **Figure 1**. Please note that as the free energies are summed as indicated by the arrows in this rectangle in **Figure 1**. This corresponds to the free energy of the oxidation process of M, which is the negative of the reduction process; to convert to potential one more sign inversion takes place such that the computed potentials in Equation (3) are standard reduction potentials, explaining the positive value of $nFE_{1/2}^0(\text{M}^{n+}/\text{M})$ in **Figure 1**.

In Equation (3), ΔG_{at}^0 is the standard atomization free energy of the metal, which can be approximated as the free energy of vaporization $\Delta G_{\text{vap}}(\text{M})$ as in **Figure 1**, because the enthalpy of fusion is small and similar (around 10-20 kJ/mol) for the metals and cancels with the entropy terms as shown below. $\Delta G_{\text{IP}}(\text{M})$ is the sum of ionization free energies that convert M to M^{n+} ; thus, e.g. if $n = 2$, the value represents the sum of the first and second ionization free energies of M. Equation (3) includes a correction to the relative scale of the desired reference electrode, in this case $\text{SHE} = +4.44$ V, which includes the surface potential χ^{S} . This corresponds to the cycle by Trasatti, because he uses $\mu(\text{H}^+)(\text{aq})$ from Equation (1) and $\text{SHE} = +4.31$ V, i.e. without χ^{S} , which cancels out in Equation (3). One can convert between the thermochemical and operational electrode potentials by using +4.31 V instead of +4.44 V, to make the tabulated ΔG_{hyd} values 13 kJ/mol smaller. Other choices can be made for $\Delta G_{\text{hyd}}(\text{H}^+)$ and can easily be used to calculate revised ΔG_{hyd} from the data presented here. Notably, if the interest is in conventional free energies of hydration ($\Delta G_{\text{hyd}}(\text{H}^+) = 0$), the value $-1100 n$ kJ/mol should be subtracted

from the tabulated data. In computational chemistry, $\mu(\text{M}^{n+})(\text{aq})$ is typically estimated rather than $\Delta G_{\text{hyd}}(\text{M}^{n+})$ due to the absence of a surface potential effect, and thus SHE = +4.31 V should be used.

Many values of $E_{1/2}^0(\text{M}^{n+}/\text{M})$ and $\Delta G_{\text{hyd}}(\text{M}^{n+})$ are known, but even more ionization potentials are available at very high accuracy in the NIST database. Errors arising from the cycle are mainly due to the errors in ΔG_{at}^0 , and $\Delta G_{\text{hyd}}(\text{M}^{n+})$. For $\Delta G(\text{IP}_n, \text{M})$ the only error is caused by the entropy of ionization that converts the ionization energies into free energies. This entropy amounts to a few kJ/mol at 298 K and can thus be neglected.³⁷ A second error relates to the estimation of ΔG_{at}^0 , as these data are not generally available. However, the enthalpies of vaporization, ΔH_{vap} are widely known and tabulated.⁴³ They are shown below to be an excellent proxy of ΔG_{at}^0 , mainly due to the small enthalpies of fusion that cancel with the entropy of fusion and the entropy of vaporizing the metal (ΔS_{vap}), which is also small and very similar for most metals; this fact is commonly referred to as Trouton's rule.⁵⁰ These cancellations are very useful as shown below. Inclusion or neglect of the Trouton entropy ($\Delta S_{\text{vap}} = 10.5 \text{ R}$ corresponding to $T\Delta S_{\text{vap}} = 0.27/n \text{ V}$ at 298 K) gives similar small mean signed errors but of opposite signs, quantifying the cancellation of error. Because of these various cancellations, Equation (4),

$$E_{1/2}^0(\text{M}^{n+}/\text{M}) = (\Delta H_{\text{vap}} + \text{IP}_n(\text{M}) + \Delta G_{\text{hyd}}(\text{M}^{n+}))/nF - 4.44 \text{ V} \quad (4)$$

applies with errors averaging to only 10 kJ/mol (0.1 V) as shown by explicit application below. From this useful equation, any missing quantity can be calculated if the remaining quantities are available. In this work, we show first the validity of Equation (4) and then use it to derive values of $\Delta G_{\text{hyd}}(\text{M}^{n+})$ that have not previously been reported in the literature, and to correct some values that have been reported.

Data used. Values of $E_{1/2}^0$ were taken from the CRC Handbook⁵¹ and from Bratsch.⁵² Data can be found in Supporting Information, **Table S1** for M^{3+} ions and **Table S2** for M^{2+} ions. The values for ΔH_{vap} were taken as reported in the Chemistry Data Book⁵³ and validated by Zhang et al.⁴³ The ΔG_{hyd} used for testing the approximation of Equation (4) were the recently derived values³⁵ that are thermochemically consistent, i.e. the values for each metal agree with their thermochemical cycles.

The experimental data may in some cases relate to a mixture of species or a species that differs from other hydrated species although all of them are referred to as " $\text{M}^{n+}(\text{aq})$ ". All data in this work accordingly also refers to the real species or mixtures. A notable example is the deprotonation of a water of the first coordination shell of the M^{3+} ions caused by the Brønsted acidity of these aqua complexes, and the hydrolytic instability and possibly mixed nature of some species such as $\text{Co}^{3+}(\text{aq})$.⁵⁴ Since all data reported here are based on the active species in solution that give rise to the observed values, this does not affect the accuracy of the tabulated data. However, variations in chemical composition and coordination number will potentially weaken the trend chemistry⁵⁵ as discussed further below. In

addition, the fact that data refer to the real species during measurement, not necessarily a single species, should be considered when estimating these values by computational chemistry.

Results and Discussion

Test of the validity of the applied approximation. The approximation of using ΔH_{vap} as in Equation (4) can be directly tested by applying Equation (4) to cases of M where all values in Equation (4) are known. **Figure 2** shows this relationship for all the M^{3+} and M^{2+} ions for which data were found. The cycle-consistent values of $\Delta G_{\text{hyd}}(M^{n+})$ were used³⁵. It should be noted that the choice of reference SHE and $\Delta G_{\text{hyd}}(H^+)$ will not affect the trend agreement (R^2) in **Figure 2**. The accuracy of the approximated cycle emerges from the standard error of the linear regression. The test includes 28 M^{3+} ions and 33 M^{2+} ions. The data can be found in Supporting Information, **Table S3 and Table S4**.

To understand the impact of the entropy of vaporization on the quality of the approximation, the linear regression was performed both with and without application of Trouton's rule.⁵⁰ When included, a value of 10.5 R, corresponding to 0.27/n V at 298.15 K (the Trouton entropy of vaporization measured as a potential) was subtracted from the calculated $E_{1/2}^0(M^{n+}/M)$ of Equation (4). **Figure 2A** shows the relation between experimental values of $E_{1/2}^0(M^{2+}/M)$ (in V) and those calculated from Equation (4) for the M^{2+} ions if the ΔH_{vap} is not included. For comparison, **Figure 2B** shows the same relation when ΔH_{vap} is included, using Equation (4) in full. **Figure 2C** uses Equation (4) completely as in **Figure 2B** but includes the Trouton entropy correction. **Figure 2D-2F** show the same relationships for the M^{3+} ions.

As seen from **Figure 2**, regardless of the metal oxidation state, Equation (4) adequately describes the experimental standard reduction potentials. The use of the enthalpies of vaporization improves the trend agreement from $R^2 = 0.83$ for M^{2+} ions and 0.94 for M^{3+} ions when the term is disregarded (**Figure 2A, 2C**) to $R^2 = 0.99$ –1.00 when included (**Figure 2B, 2D**). For the M^{2+} ions, the mean absolute error (MAE) without considering $\Delta G_{\text{at}}^0/\Delta H_{\text{vap}}$ is 1.24 V, with a mean signed error (MSE) of -1.24 V. For the M^{3+} ions, the MAE is 0.98 V and MSE is -0.98 V. Accordingly, for both oxidation states the neglect of the atomization free energy produces too small reduction potentials of ~ 1 V, because this free energy is always positive and dominated by ΔH_{vap} , as it reflects the breaking of the metal-metal bonds. The Trouton entropy compensates this somewhat by favoring release of the metal atoms to the gas state. Complete neglect of ΔG_{at}^0 thus favors reaction towards the right in **Figure 1**, away from the reduced metal state. In an electrochemical measurement, the energy required to release the metal atoms from the bulk metal during the oxidation process is thus a major contributor to the observed potentials.

Figure 2. **A)** Relation between $E_{1/2}^0$ (in V) and $E_{1/2}^0$ calculated from the IPs and ΔG_{hyd} for M^{2+} ions. **B)** Relation using a thermochemical cycle that includes ΔH_{vap} . **C)** Same as B) but included an entropy correction based on Trouton's rule. **D)** Same as A) for M^{3+} ions. **E)** Same as B) for M^{3+} ions. **F)** Same as C) for M^{3+} ions. All values used are experimental (directly or derived by thermochemical cycles).

When one includes ΔH_{vap} and uses Equation (4) specifically (**Figure 2B, 2D**), $\text{MES} = -0.04$ V and $\text{MAE} = 0.10$ V for M^{2+} ions, and $\text{MSE} = -0.05$ V and $\text{MAE} = 0.08$ V for the M^{3+} ions. Because the systematic error is of the order of chemical accuracy, the approximation of using Equation (4) directly is adequate. The reason largely relates to the fact that ΔS_{vap}^0 is similar for all metals, consistent with Trouton's rule⁵⁰. To see this, inclusion of the Trouton entropy in **Figure 2C** and **2F** does not change trend agreement and does not improve numerical accuracy ($\text{MAE} = 0.12$ V and 0.08 V for M^{2+} and M^{3+} ions, respectively, **Table S3** and **Table S4**). Because ΔS_{vap}^0 reduces slightly the positive free energy of vaporization, the signed error becomes of similar magnitude but with opposite sign (0.04 - 0.10 V). The remaining error arises from the gas phase ionization entropy of a few kJ/mol at 298 K, as discussed by Trasatti³⁷. Considering the experimental measurement uncertainty and the uncertainty in the choice of reference $\Delta G_{\text{hyd}}(\text{H}^+)$, this minor correction does not affect the accuracy of the absolute potentials, and fully cancels out in the trend chemistry (i.e. relative potentials and relative free energies of hydration).

Table 1. Free energies of hydration for M³⁺ ions (kJ/mol).

	Marcus ^{33,34}	Marcus ⁸	Noyes ²⁹	Fawcett ^{31,b}	Rizkalla & Choppin ³²	Kepp ³⁵	This work
Ac ³⁺	N/A	-3179	N/A	N/A	N/A	N/A	-3086
Ag ³⁺	N/A	N/A	N/A	N/A	N/A	-4683	
Al ³⁺	-4525	-4554	N/A	-4662	N/A	-4657	
Au ³⁺	-4420	N/A	N/A	N/A	N/A	-4324	
Bi ³⁺	-3480	-3508	N/A	N/A	N/A	-3612	
Ce ³⁺	-3200	N/A	N/A	N/A	-3240	-3332	
Co ³⁺	-4495	-4527	N/A	N/A	N/A	-4622	
Cr ³⁺	-4010	-4517	-4339	-4531	N/A	-4536	
Cu ³⁺	N/A	N/A	N/A	N/A	N/A	-4979	
Dy ³⁺	-3425	-3457	N/A	N/A	-3481	-3557	
Er ³⁺	-3495	-3523	N/A	N/A	-3537	-3627	
Eu ³⁺	-3360	-3395	-3527	N/A	-3397	-3476	
Fe ³⁺	-4265	-4296	-4335	-4416	N/A	-4383	
Ga ³⁺	N/A	-4542	N/A	-4670	N/A	N/A	-4654
Gd ³⁺	N/A	-3411	N/A	N/A	-3421	N/A	-3415/-3500 ^b
Ho ³⁺	-3470	-3493	N/A	N/A	-3510	-3602	
In ³⁺	-3980	-4012	-4100	-4121	N/A	-4112	
Ir ³⁺	N/A	N/A	N/A	N/A	N/A	N/A	-4150
La ³⁺	-3145	-3176	N/A	N/A	-3193	-3277	
Lu ³⁺	N/A	-3545	N/A	N/A	-3609	N/A	-3698
Mn ³⁺	N/A	N/A	N/A	N/A	N/A	-4520	
Mo ³⁺	N/A	N/A	N/A	N/A	N/A	N/A	-4250
Nb ³⁺	N/A	N/A	N/A	N/A	N/A	N/A	-4165
Nd ³⁺	-3280	-3308	N/A	N/A	-3311	-3412	
Ni ³⁺	N/A	N/A	N/A	N/A	N/A	-4813	
Np ³⁺	N/A	N/A	N/A	N/A	N/A	N/A	-3203
Os ³⁺	N/A	N/A	N/A	N/A	N/A	N/A	-4000
Pa ³⁺	N/A	N/A	N/A	N/A	N/A	N/A	-3084
Pm ³⁺	-3250	-3328	N/A	N/A	-3341	-3382	-3430 ^c
Pr ³⁺	-3245	-3273	N/A	N/A	-3278	-3377	
Pu ³⁺	-3235	N/A	N/A	N/A	N/A	-3367	
Re ³⁺	N/A	N/A	N/A	N/A	N/A	N/A	-4298
Rh ³⁺	N/A	N/A	N/A	N/A	N/A	N/A	-4450
Ru ³⁺	N/A	N/A	N/A	N/A	N/A	N/A	-4295 ^d
Sc ³⁺	-3795	-3824	N/A	-3933	N/A	-3927	
Sm ³⁺	-3325	-3353	N/A	N/A	-3370	-3456	
Ta ³⁺	N/A	N/A	N/A	N/A	N/A	N/A	-4162
Tb ³⁺	N/A	-3435	N/A	N/A	-3450	N/A	-3549
Tc ³⁺	N/A	N/A	N/A	N/A	N/A	N/A	-4170 ^e
Ti ³⁺	-4015	N/A	-4046	N/A	N/A	-4147	
Tl ³⁺	N/A	-3996	N/A	-4122	N/A	N/A	-4102
Tm ³⁺	-3515	-3545	N/A	N/A	-3563	-3647	
U ³⁺	-3205	-3306	N/A	N/A	N/A	-3337	
V ³⁺	-4220	-4285	N/A	N/A	N/A	-4338	
W ³⁺	N/A	N/A	N/A	N/A	N/A	N/A	-4306
Y ³⁺	N/A	-3450	N/A	N/A	-3497	N/A	-3523
Yb ³⁺	-3570	-3494	N/A	N/A	-3587	-3688	

^a Values by Fawcett were converted from conventional data using $\Delta G_{\text{hyd}}(\text{H}^+) = -1100 \text{ kJ/mol}$. ^b -3415 kJ/mol from Equation (4) is too large as seen from the lanthanide trend, probably due to error in ΔH_{vap} ; -3500 kJ/mol is estimated from the trend. ^c The value previously reported³⁵ was based on an older number by Marcus (-3250 kJ/mol), converted to $\Delta G_{\text{hyd}}(\text{H}^+) = -1100 \text{ kJ/mol}$. The new value is his 2015 value (-3328 kJ/mol) converted from $\Delta G_{\text{hyd}}(\text{H}^+) = -1056$ to -1100 kJ/mol, giving -3430 kJ/mol with good trend behavior. ^d Computed from $E(\text{Ru}^{3+}/\text{Ru}^{2+}) = +0.24 \text{ V}$ ⁵² and the value -2000 kJ/mol for Ru^{2+} found from Equation (4). ^e Same, using $E(\text{Tc}^{3+}/\text{Tc}^{2+}) = +0.3 \text{ V}$.

Table 2. Free energies of hydration for M²⁺ ions (kJ/mol).

	Marcus ^{33,34}	Marcus ⁸	Noyes ²⁹	Fawcett ^{31,a}	Rizkalla & Choppin ³²	Kepp ³⁵	This work
Ag ²⁺	-1865	N/A	N/A	N/A	N/A	-1953	
Au ²⁺	N/A	N/A	N/A	N/A	N/A	-1954	
Ba ²⁺	-1250	-1270	-1314	-1343	N/A	-1338	
Be ²⁺	-2395	-2417	-2436	-2489	N/A	-2483	
Ca ²⁺	-1505	-1527	-1588	-1599	N/A	-1593	
Cd ²⁺	-1755	-1748	-1795	-1820	N/A	-1843	
Co ²⁺	-1915	-1936	-2013	-2008	N/A	-2003	
Cr ²⁺	-1850	-1841	-2013	-1924	N/A	-1938	
Cu ²⁺	-2010	-2028	-2076	-2100	N/A	-2086	
Dy ²⁺	N/A	N/A	N/A	N/A	-1463	-1526	
Er ²⁺	N/A	N/A	N/A	N/A	-1495	-1576	
Eu ²⁺	-1385	-1409	N/A	N/A	-1409	-1473	
Fe ²⁺	-1840	-1864	-1890	-1949	N/A	-1928	
Ge ²⁺	N/A	N/A	N/A	N/A	N/A	N/A	-1726
Hg ²⁺	-1760	-1778	-1820	-1850	N/A	-1848	
Ho ²⁺	N/A	N/A	N/A	N/A	-1480	-1561	
In ²⁺	N/A	N/A	N/A	N/A	N/A	-1787	
Mg ²⁺	-1830	-1837	-1900	-1922	N/A	-1918	
Mn ²⁺	-1760	-1787	-1826	-1859	N/A	-1848	
Nd ²⁺	N/A	N/A	N/A	N/A	-1360	-1448	
Ni ²⁺	-1980	-2014	-2062	-2087	N/A	-2068	
Pb ²⁺	-1425	-1510	-1492	-1518	N/A	-1513	
Pd ²⁺	-1910	-1957	-2397	N/A	N/A	-1998	
Pm ²⁺	N/A	N/A	N/A	N/A	-1378	-1394	
Po ²⁺	N/A	N/A	N/A	N/A	N/A	N/A	-1848
Pr ²⁺	N/A	N/A	N/A	N/A	-1342	-1420	
Pt ²⁺	-1960	-1969	N/A	N/A	N/A	-2048	
Pu ²⁺	N/A	N/A	N/A	N/A	N/A	N/A	-1489 ^b
Ra ²⁺	-1250	-1271	-1280	N/A	N/A	-1338	
Ru ²⁺	N/A	N/A	N/A	N/A	N/A	N/A	-2000
Sc ²⁺	N/A	N/A	N/A	N/A	N/A	N/A	-1745 ^c
Sm ²⁺	-1375	-1388	N/A	N/A	-1394	-1463	
Sn ²⁺	-1490	-1504	-1554	-1581	N/A	-1578	
Sr ²⁺	-1380	-1398	-1421	-1470	N/A	-1468	
Tc ²⁺	N/A	N/A	N/A	N/A	N/A	N/A	-1776
Ti ²⁺	N/A	N/A	-1782	N/A	N/A	-1887	
Tm ²⁺	N/A	N/A	N/A	N/A	-1509	-1580	
V ²⁺	-1825	-1602	-1845	N/A	N/A	-1913	
Yb ²⁺	-1510	-1523	N/A	N/A	-1523	-1598	
Zn ²⁺	-1955	-1975	-2022	-2048	N/A	-2043	

^a Values reported by Fawcett were converted from conventional data using $\Delta G_{\text{hyd}}(\text{H}^+) = -1100 \text{ kJ/mol}$. ^b From the value for Pu³⁺ (-3367) and $E(\text{Pu}^{3+}/\text{Pu}^{2+}) = -2.80 \text{ V}$.⁵² ^c From the value for Sc³⁺ (-3927) and $E(\text{Sc}^{3+}/\text{Sc}^{2+}) = -2.30 \text{ V}$.⁵²

New free energies of hydration. Considering the accuracy of Equation (4), we can now apply it to deduce values of ΔG_{hyd} for metal ions not reported previously in the literature, and we can also use the equation to test the thermochemical consistency (i.e. cycle-consistency) of previously reported values of ΔG_{hyd} . **Table 1** and **Table 2** show the new values of ΔG_{hyd} compared with values of ΔG_{hyd} values previously reported. For many of the data, the differences lie mainly in the choice of reference values for SHE and the hydration free energy of the proton, as discussed above. Thus, the relative values for two ions, in particular of the same oxidation state, are often similar for the new and old reported data, which is another illustration of the validity of Equation (4). These relative differences are chemically very important because they contribute substantially to the comparative chemistry, e.g. the selectivity of the ions towards host molecules in aqueous solution.^{11,12}

Taking just one example, the difference in ΔG_{hyd} for Ca^{2+} and Cd^{2+} , which is biologically important, is 250 kJ/mol for the original data of Marcus³⁴ and the cycle-consistent values previously calculated³⁵, but it is only 221 kJ/mol when estimated from the data by Fawcett³¹ and the newer compilation by Marcus,⁸ and only 207 kJ/mol using the data compiled by Noyes²⁹, thus giving a spread in the relative ΔG_{hyd} of 43 kJ/mol, which is clearly unacceptable. We do not know which values are correct. However, using the values that we reported previously (-1593 kJ/mol for Ca^{2+} ; -1843 kJ/mol for Cd^{2+})³⁵ produces $E_{1/2}^0(\text{M}^{n+}/\text{M})$ of -2.91 V (-2.77 V if including the Trouton entropy), i.e. an error of 0.04 V (4 kJ/mol) vs. the experimental potential of -2.87 V when using Equation (4) and the consensus $\Delta H_{\text{vap}} = 153$ kJ/mol for Ca^{2+} . If the value -1593 kJ/mol is in error, it must be caused by ΔH_{vap} also being wrong,⁴³ as the entropy contributions are too small to make a difference. For Cd^{2+} , application of Equation (4) using $\Delta H_{\text{vap}} = 100$ kJ/mol with the Trouton entropy gives -0.39 V, without it gives -0.52 V, compared to the experimental -0.40 V, suggesting an error in the relative ΔG_{hyd} of ~12 kJ/mol.

Using the thermochemical cycle of Equation (4) as a test of accuracy, errors larger than 0.2 V are found for Ho^{2+} (-0.23 V), Pm^{2+} (0.30 V), Ra^{2+} (-0.28 V), and U^{3+} (-0.33 V), which can be considered particularly uncertain. This probably relates to errors in the measurements of the heats of vaporization, as discussed previously⁴³, or to these metals deviating from Trouton's rule regarding ΔS_{vap}^0 . In this context it is interesting that all these four metals are very heavy ($Z \geq 61$). As more accurate data arrive at higher accuracy, the cycle and approximation in Equation (4) will probably become more valuable.

Among the new values identified in this work, those of the M^{3+} ions of the 4d and 5d transition series are particularly interesting. The new free energies of hydration for 4d metal ions include Nb^{3+} (-4165 kJ/mol), Mo^{3+} (-4250 kJ/mol), Tc^{2+} (-1776 kJ/mol), Ru^{2+} (-2000 kJ/mol), and Rh^{3+} (-4450 kJ/mol). The 5d metal ions include Ta^{3+} (-4162 kJ/mol), W^{3+} (-4306 kJ/mol), Re^{3+} (-4298 kJ/mol), and Ir^{3+} (-4150

kJ/mol). Many of these are important to homogenous catalysis and in materials, but are also important in their own right for understanding the 4d and 5d trend chemistry.

As an example, $\text{Ir}^{3+}(\text{aq})$ is one of the most inert systems in water with an extremely slow exchange of water ligands⁵⁶ and has been studied in detail both theoretically and experimentally.⁵⁷ While one expects ΔG_{hyd} to correlate with the lifetime of the complex (stronger hydration for higher charge and ligand field stabilization also gives slower ligand exchange), the new value in Table 1 of -4150 kJ/mol is not remarkably high in comparison to other M^{3+} ions, and thus the special inertness of $\text{Ir}^{3+}(\text{aq})$, which is a kinetic rather than thermodynamic phenomenon, has to be due to other features of the ion.

It is also worth noticing the experimentally elusive, highly unstable ($E(\text{Sc}^{3+}/\text{Sc}^{2+}) = -2.30 \text{ V}$) but theoretically interesting Sc^{2+} with $[\text{Ar}]3\text{d}^1$ configuration. Sc^{2+} has $\Delta G_{\text{hyd}} = -1745 \text{ kJ/mol}$, which is well in trend with ΔG_{hyd} for Ti^{2+} (-1887 kJ/mol) and V^{2+} (-1913 kJ/mol).

Main anomalies. Anomalies can be identified from the trend chemistry. Whereas the variations in the gas phase are exclusively due to electronic structure of the bare ions and atoms, variations in chemical composition of the hydrated states are possible. Such variations may affect the trends resulting from the effective nuclear charge and d/f-orbital occupation beyond the errors of the experimental data of the cycle and should thus be considered separately.

For the lanthanide $\Delta G_{\text{hyd}}(\text{M}^{3+})$ series, ΔG_{hyd} for Gd^{3+} is -3415 kJ/mol when computed using the cycle with the consensus ΔH_{vap} of 302 kJ/mol.⁴³ This ΔG_{hyd} value is irregular by not following a smooth linear decrease in $\Delta G_{\text{hyd}}(\text{M}^{3+})$ (Supporting Information, **Figure S1**). From this, and trusting the measured ionization potentials listed in NIST, one can conclude that either the reduction potential or ΔH_{vap} of Gd is incorrect. The electronic structures, sizes, and reduction potentials are similar, and thus the chemical composition is also expected to be similar for the lanthanides, except a change in effective hydration number from 9 to 8 in the series. Accordingly, the ΔH_{vap} of Gd is the most likely reason for the discrepancy, one can estimate a value of ΔH_{vap} is 400 kJ/mol, 100 kJ/mol more than the currently accepted value, assuming that the reduction potential is correctly reported.

Also using the trend as quality control, the tabulated ΔG_{hyd} for Yb^{3+} by Marcus of -3494 kJ/mol should probably be corrected to $-3570 \pm 10 \text{ kJ/mol}$ on his scale,⁸ and the value for Lu^{3+} of -3545 kJ/mol should be close to -3600 kJ/mol on the same scale. Similarly, the value for Pd^{2+} tabulated by Noyes (-573 kcal/mol = -2397 kJ/mol)²⁹ is substantially too negative by 400 kJ/mol or so, and is probably a misprint that should have been -473 kcal/mol.

Figure 3. Trends in thermochemically consistent hydration free energies of M^{3+} ions of **A)** the 3d transition series; **B)** the 5d transition series; **C)** the 4d transition series; **D)** the lanthanides.

Among other interesting variations, the new value for Ru^{2+} (-2000 kJ/mol) is 72 kJ/mol smaller than ΔG_{hyd} for Fe^{2+} (-1928 kJ/mol). However, the new value for Tc^{2+} (-1776 kJ/mol) is 72 kJ/mol less negative than the value for Mn^{2+} (-1848 kJ/mol). This curious difference is not due to a relative change in d-orbital occupation and ligand field stabilization energy, as the change from high-spin Mn^{2+}/Fe^{2+} to low-spin Tc^{2+}/Ru^{2+} is similar. The t_{2g}^6 state of Ru^{2+} is of course particularly stable but whereas the 3d ions are invariably 6-coordinated, the assumption of pseudo-octahedral geometry may break down for the 4d ions because coordination numbers are variable and not generally well established^{8,55}, potentially explaining this difference. The Ru^{2+}/Ru^{3+} potential has been studied using the standard Born Haber cycle for $M^{2+/3+}$.⁵⁸ It was estimated that $\Delta G_{hyd}(Ru^{3+}) - \Delta G_{hyd}(Ru^{2+})$ is ~ 24 eV or about 2315 kJ/mol. Using the new value for Ru^{2+} (-2000 kJ/mol) and the potential of +0.24 V by Bratsch⁵², one calculates $\Delta G_{hyd}(Ru^{3+}) = -4295$ kJ/mol, which has been included in **Table 1**. This gives an experimental difference in ΔG_{hyd} of 2295 kJ/mol, the minor difference being due to the choice of SHE (4.44 V vs. 4.28 V⁵⁸).

Trend chemistry. It is important to understand the periodic trends in the properties of metal ions. When both M^{2+} and M^{3+} values of ΔG_{hyd} are available, the contribution of the difference in $\Delta G_{hyd}(M^{3+}) - \Delta G_{hyd}(M^{2+})$ to the chemically important $E_{1/2}^0(M^{3+}/M^{2+})$ potential can be assessed. Previous

analysis suggests that the variations in $\Delta G_{\text{hyd}}(\text{M}^{3+}) - \Delta G_{\text{hyd}}(\text{M}^{2+})$ (the hydration energy effects) contributes to the same extent to the variation in $E_{1/2}^0(\text{M}^{3+}/\text{M}^{2+})$ as the variations in the ionization potentials (electronic structure) of the gas-phase atomic M. At first instance, this seems unsurprising since they are both large in energy terms. However, the variations in ionization energy and $\Delta G_{\text{hyd}}(\text{M}^{3+}) - \Delta G_{\text{hyd}}(\text{M}^{2+})$ hide important ligand field effects that contribute to the net observed potential; thus for example, the $\Delta G_{\text{hyd}}(\text{M}^{3+})$ and $\Delta G_{\text{hyd}}(\text{M}^{2+})$ trends have their humps shifted due to the difference of one d-electron, which changes the position of the maximal and minimal ligand field stabilization energy^{35,59}. Variations in the relative importance of $\Delta G_{\text{hyd}}(\text{M}^{3+}) - \Delta G_{\text{hyd}}(\text{M}^{2+})$ and the differential ionization energy thus relate strongly to the different electronic splitting of bare atomic ions vs. octahedral aqueous ions. For larger ions, such analysis is complicated by coordination numbers larger than 6.

Figure 3 shows the thermochemically consistent values of $\Delta G_{\text{hyd}}(\text{M}^{3+})$ for the 3d, 4d, 5d, and lanthanide transition series, including both the new values obtained in this work and the recently reported values.³⁵ Since these values (the last two columns of **Table 1** and **Table 2**) are all thermochemically consistent (consistent with their respective thermochemical cycles and using the same reference states), they can be applied to trend chemistry as done in **Figure 3**. The corresponding trends for the 3d and 4d series of the M^{2+} ions are shown in **Figure S2** and **Figure S3**, respectively, showing how Sc^{2+} fits excellently in the overall trend, and showing the expected trend of Tc^{2+} and Ru^{2+} in the 4d series. The overall trends follow the patterns seen for enthalpies of hydration, such as $\Delta H_{\text{hyd}}(\text{M}^{2+})$ ⁶⁰, due to the similar hydration entropy of the species, which is dominated by the vibrational entropy of the M-O bonds of the first solvation sphere.

Among the most interesting observations from **Figure 3** is i) the generally expected observation that the hydration free energy becomes more negative with increasing effective nuclear charge towards the right of each series. ii) that this tendency becomes less pronounced from 3d to 4d (**Figure 3A-3C**), from 4d to 5d (**Figure 3B-3C**), and from 5d to the lanthanides (**Figure 3B-3D**). Thus the $\Delta G_{\text{hyd}}(\text{M}^{3+})$ lanthanides vary by only 420 kJ/mol from La to Lu, and the trend is very linear, showing that variations in properties and chemical composition are minor for this series (**Figure 3D**). Illustrating this point, most lanthanides having $E_{1/2}^0(\text{M}^{3+}/\text{M})$ of -2.3 V. The notable exception and major outlier is Eu with $E_{1/2}^0(\text{M}^{3+}/\text{M})$ of -1.99 V.⁵² iii) The trends of the three d-transition series trend are all disrupted by a hump of approximately 100 kJ/mol in the middle of the series, which is due to d-orbital occupation effects. Specifically, for the 3d series (**Figure 3A**), the hump occurs with a local minimum at Cr^{3+} , which has t_{2g}^3 configuration and thus maximal ligand field stabilization energy for the high-spin aqua ions in the pseudo-octahedral (O_h) ligand field of the first solvation sphere. Accordingly, the local maximum occurs

at Fe^{3+} , which has zero ligand field stabilization energy ($t_{2g}^3e_g^2$). These findings are well in line in expectations from quantum chemical calculations.⁵⁹

$\text{Co}^{3+}(\text{aq})$ generally thought to be the only low-spin ion of the 3d series, and $\text{Rh}^{3+}(\text{aq})$ is accordingly clearly low-spin. However it has been argued that high-spin $\text{Co}^{3+}(\text{aq})$ is actually measured under most conditions, based on analysis of spin-crossover entropies, ligand substitution reactions and self-exchange electron transfer.⁵⁴ **Figure 3A** supports our previous claim⁵⁴ that $\text{Co}^{3+}(\text{aq})$ is in a high-spin state as measured, since $\text{Co}^{3+}(\text{aq})$ falls near the background linear trend of the effective nuclear charge with the additional ligand field effect in good trend with Fe^{3+} , Ni^{3+} , and Cu^{3+} , which are high-spin (for Cu^{3+} this makes no difference as it has $t_{2g}^6e_g^2$ configuration regardless of the ligand field strength). The value for Os^{3+} is very high (**Figure 3B**) considering that it has higher effective nuclear charge and more occupied bonding d-orbitals than the metal ions preceding it in the series. In fact, low-spin assumption of the 5d series would imply only one hump at t_{2g}^6 (Ir^{3+}) vs. two for the high-spin 3d metal ions. The 5d series looks more like a high-spin than a low-spin series, and changes in chemical composition or solvation number⁵⁵ may happen from $\text{W}^{3+}/\text{Re}^{3+}$ to Os^{3+} if the heats of vaporization are accurate. 4d and 5d metal ions such as rhodium and molybdenum are known to form cluster aqua ions, and we thus note that the data for the 5d metal ions are overall the most scarce and uncertain.

Again, **Figure 3C** reveals the $\text{Ru}^{3+}/\text{Tc}^{3+}$ anomaly that was also apparent from group-wise comparison, with the maximum occurring period-wise already at Tc^{3+} vs. Ru^{3+} which would be expected for six-coordination. Considering the accuracy of the data, this suggests a change in geometry of electronic structure occurring at Tc^{3+} . Two main possibilities can be envisioned: One is a change in solvation number and thus d-orbital stabilization effects occurring with Tc^{3+} , i.e. that this ion has a higher coordination number than 6. The other possible explanation is that $\text{Tc}^{3+}(\text{aq})$ is in a strongly Jahn-Teller distorted high-spin d^4 state, while the later ions of the series are low-spin. The fact that Jahn-Teller distortion would stabilize the high-spin state of $\text{Tc}^{3+}(\text{aq})$ to make it the perhaps only $\text{M}^{3+}(\text{aq})$ high-spin state of the 4d series is worth exploring further. The same occurs for $\text{Mn}^{3+}(\text{aq})$ of course, but in this case the neighbor ions are all high-spin thus making the Jahn-Teller effect on the trend smaller.

Main determinants of redox stability of metal ions in water. With the consistent data now available in **Table 1** and **Table 2**, we can address a final, important question of how the observed standard reduction potentials $E_{1/2}^0(\text{M}^{n+}/\text{M})$, which determine the relative activity and stability of the metal ions in water, are caused by contributions from the three terms of Equation (4). In this consideration the effect of the ionization energy represents the intrinsic vacuum electronic structure contribution to $E_{1/2}^0(\text{M}^{n+}/\text{M})$, with a larger value reflecting more stable electrons in the metal atom, favoring reduction.

the heat of vaporization represents the intrinsic stability of the bulk metal material via the metal-metal bonding strength. These two terms are always positive and favor reduction to the metal state. The last term, the free energy of hydration, represents the oxidized ion's affinity for the water phase in the electrochemical system, is always negative and favors oxidation. As evident from the analysis in this work, despite the range of tens of eV in the ionization and hydration free energies, the latter term almost completely cancels the first two terms to give standard reduction potentials of only ± 3 V.

Figure 4. **A)** Contributions of ionization energy, free energy of hydration, and vaporization enthalpy to the standard reduction potentials of M^{2+} ions. **B)** Same for M^{3+} ions. **C)** Relation between ionization energy and hydration free energy for M^{2+} ions. **D)** same for M^{3+} ions. Notable outliers are main group elements and noble metals as marked.

To understand the important variations in this overall tendency, the exact contribution for each metal is summarized in **Figure 4**, using the data in Supporting information **Table S1** and **Table S2**. **Figure 4A** shows the contributions for the M^{2+} ions, whereas **Figure 4B** shows them for the M^{3+} ions. The metal ions have been ordered according to the electrochemical (activity) series specific to each

oxidation state, i.e. according to $E_{1/2}^0(M^{n+}/M)$. The correlation between the ionization potentials and the hydration free energies are very evident as seen from **Figure 4C** and **4D**. In contrast, ΔH_{vap} does not correlate with ionization energies at all (**Figure S4**). Accordingly, we can conclude that ΔH_{vap} , which measures the metal self-affinity or metal stability, is a very important determinant of deviations from the expected trends in reduction potentials; these contributions are colored gray in **Figure 4A** and **4B**. It can be seen that outliers from the trends are mainly due to main group elements and noble metals.

This analysis helps understand why Eu^{3+} has a substantially less negative $E_{1/2}^0(M^{3+}/M) = -1.99 \text{ V}$ than the remaining lanthanides (typically -2.3 V). **Figure S5** shows the correlation between ionization energy and ΔG_{hyd} for the lanthanides, showing that Eu^{3+} and Lu^{3+} in the middle and end of the series are outliers in this relationship, which is certainly an f-orbital occupation effect in the water ligand field distinct from the bare ion. One would expect from the linear relationship alone that Eu^{3+} had a 200 kJ/mol more negative hydration free energy considering its ionization energy. The reason is, arguably, a combination of the change in solvation number from 9 to 8 in the lanthanide series combined with a low ligand field stabilization energy of the split f-orbitals in the field of the high coordination number.

As another illustrative example, Sc^{3+} (-2.08 V) and Pu^{3+} (-2.03 V) have very similar aqueous reduction potentials but for extremely different reasons. While they have very similar metal vaporization enthalpies, for Sc the ionization energy required to produce the trivalent ion from the metal is 5.5 eV larger than for Pu; in contrast the hydration free energy is about 5.8 eV less negative for Pu^{3+} than for Sc^{3+} , such that the two tendencies almost cancel. In other words, there are two completely different ways to attain a similar reduction potential, a fact that may be of interest to the rational design of electrocatalysts.

Conclusions

In an electrochemical measurement, the energy required to release the metal atoms from the bulk metal during the oxidation process is a major contributor to the observed potentials. However, this free energy can be described accurately by the enthalpy of vaporization of the metal, partly because the entropy of vaporization is relatively small and similar for most metals, a fact known as Trouton's rule. This principle has been used in the present paper to calculate many new, thermochemically consistent free energies of hydration of M^{3+} and M^{2+} ions, which add to the previously reported values. The values are shown to be accurate with a trend accuracy of $R^2 = 0.99\text{-}1.00$ and a numerical accuracy of $\sim 10 \text{ kJ/mol}$. Some implications and trends of the new values and their contributions from each term in the cycle of

Equation (4) are discussed. It is hoped that the new values and the relationships identified will be of value in future studies of these metal ions and their aqueous chemistry.

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Supporting Information. The Supporting Information file contains data with experimental standard half reduction potentials (in V) and first, second, and third ionization potentials (in eV) used for the calculations done in this work.

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Table of Content Graphic

Figure 1

118x44mm (300 x 300 DPI)

Figure 2

363x228mm (300 x 300 DPI)

Figure 3

218x132mm (300 x 300 DPI)

Figure 4

321x210mm (300 x 300 DPI)

81x24mm (600 x 600 DPI)