Extension of thermodynamic database with ^{12}C and ^{13}C compounds for calculation of isotopic equilibria by Gibbs energy minimisation

Yu. A. Shibetsky
D. A. Kulik
Environmental Radiogeochemistry Centre (SSC ER), 252180
Kyiv, Ukraine

Traditional computation of equilibrium isotopic composition of compounds δ_{SP} consists in application of law of mass action (LMA) equations for finding equilibrium speciation in the system, followed by calculation of δ_{SP} values using isotopic fractionation coefficients α between compounds (Ohmoto, 1972). This may be difficult if minerals are involved into the mass balance because, with introduction of isotopes, each mineral turns into a solid solution with isotopic end-members. However, Gibbs energy minimisation algorithms (e.g.Karpov *et al.*, 1997) are capable of solving directly such systems for equilibrium quantities of isotope species if their apparent standard state Gibbs energies of formation ΔG_f^{oi} are provided. This paper presents a consistent approach to extension of thermodynamic database of ΔG_f^{o}f for aqueous species, gases and minerals with respective isotopic species, illustrated by a subset for ^{12}C and ^{13}C compounds. The extended database was tested by modelling ambient and hydrothermal aquatic systems with carbonate minerals using Selektor-A code (Kulik *et al.*, 1997).

Calculation of ΔG_f^{oi} for isotopic species

Values of ΔG_f^{oi} of carbon isotopic species were calculated using the Grichuk (1987) equations:

$$\Delta G_{fAX_o}^{oi} = \Delta G_{fAX}^{o} + N_{X*} RT \ln\alpha_{AX\text{-}X} \qquad (1)$$

$$\Delta G_{fAX*}^{oi} = \Delta G_{fAX}^{0} - N_{X_o} RT \ln \alpha_{AX\text{-}X} \qquad (2)$$

where indices X^o and X^* stand for light and heavy isotopes of element X in a compound AX; ΔG_{fAX}^{0} is apparent molar Gibbs energy of AX formation from mixed-isotope elements, $\Delta G_{fAX_o}^{oi}$ and ΔG_{fAX*}^{oi} refer to isotopic forms of AX; N_{X_o} and N_{X*} are fractions of isotopes in the bulk elemental content in the system; $\alpha_{AX\text{-}X}$ is coefficient of isotopic fractionation compound AX and element X at standard state; *R* is universal gas constant and *T* is temperature. Source ΔG_{fAX}^{o} from Selektor-A built-in thermodynamic dataset (SUPCRT-based data) were taken into calculations of $\Delta G_{fAX_o}^{oi}$ and ΔG_{fAX*}^{oi}. Values of $\alpha_{AX\text{-}X}$ for carbon compounds were recalculated using (Golyshev, 1981; Taylor, 1986 and refs. therein). *T* dependence of α was represented by an equation

$$10^3 \ln\alpha_{AX\text{-}X} = AT^{-3} + BT^{-2} + CT^{-1} + D \qquad (3)$$

To ensure consistency of calculated ΔG_{fAX}^{oi} at elevated *TP*, instead of re-fitting $C_p = f(T)$ or HKF EOS parameters, a special procedure was implemented, based on 'pseudo-reactions' AX = AX^o and AX = AX^* in REACDC data format of Selektor-A database. At *TP*, first, $\Delta G_{fAX,T}^{o}$ is calculated from

TABLE 1. Modelled carbon isotopic composition and fractionation in the air-seawater-calcite system

Variant, Run	pH calc.	$\delta^{13}C_{SP}$,‰ $CO_{2,gas}$	HCO_3^-	CO_3^{2-}	$CaCO_{3,s}$	$10^3 \ln \alpha_{SP\text{-}CO_2}$,‰ HCO_3^-	CO_3^{2-}	$CaCO_{3,s}$
AWS-5	5.5	−6.88	+0.92	+0.13	–	+7.80	+7.01	–
AWS-6	6.7	−6.88	+1.06	+0.68	–	+7.94	+7.56	–
AWS-8	8.1	−6.87	+1.03	+0.65	+3.30	+7.90	+7.52	+10.17
WAS	8.1	−11.16	−3.56	−3.70	−1.04	+7.66	+7.46	+10.12
Ref. data		–	–	–	–	+7.7...+8.3	+7.5...+7.6	+9.8

TABLE 2. Modelled carbon isotopic composition and fractionation in the hydrothermal system

Variant,	pH	Log	$\delta^{13}C_{SP}$,‰						$10^3 \ln \alpha_{SP\text{-}CO_2}$,‰			
	calc.	f_{O_2}	CO_2	CH_4	CO_3^{2-}	HCO_3^-	$CaCO_{3,s}$	C_s	CO_3^{2-}	HCO_3^-	$CaCO_{3,s}$	$CaCO_{3,s}$
WR-33	5.7	−33.0	+0.3	–	−3.1	−5.5	−1.0	–	−3.4	−5.8	−1.3	–
WR-34	5.8	−34.0	+0.4	–	−3.0	−5.5	−0.9	–	−3.4	−5.8	−1.3	–
WR-40	5.8	−39.8	+13.5	−14.8	+10.2	+7.6	+12.2	−0.4	−3.4	−5.9	−1.3	−13.9
Ref.data			–	–	–	–	–	–	−3.3	−5.0	−1.5	−14.0

standard-state thermodynamic data and $f(T,P)$ equations. Next, values of ΔG^o_T and ΔG^*_T of both pseudoreactions are calculated from the rightmost terms of Eqns. (1,2) by substitution of α_T from Eqn.(3), to obtain values of $\Delta G^{oi}_{fAX,T}$. This procedure maintains uncertainty of $\Delta G^{oi}_{fAX,T}$ less than 0.1 J·mol^{-1} relative to $\Delta G^o_{fAX,T}$ at all TP, which corresponds to $\delta^{13}C_{SP} = \pm$ 0.1 ‰. Values of N_{X_o} and N_{X^*} were calculated from total isotopic composition of the system ($\delta^{13}C_{sys}$) using:

$$N_{X_o} = 1/(1 + R_{sys}),\ N_{X^*} = R_{sys}/(1 + R_{sys}) \qquad (4)$$

$$R_{sys} = (\delta^{13}C_{sys} * R_{PDB})/1000 + R_{PDB} \qquad (5)$$

where R_{PDB}= 0.0112372 is atomic ratio $^{13}C/^{12}C$ in PDB standard, R_{sys} is $^{13}C/^{12}C$ ratio in the system.

Numerical examples

Atmosphere-seawater equilibrium in presence of calcite at P = 1 bar and T = 25°C comprises a good test of the values $\Delta G^{oi}_{fAX_o}$ and $\Delta G^{oi}_{fAX^*}$ obtained from predicted (not experimentally measured) α because of: isotopic equilibrium between atmospheric CO_2, marine HCO_3^- and carbonate sediments; well known constancy of isotopic composition of these carbon reservoirs; and reliable experimental data on isotopic fractionation in the system CO_2-HCO_3^--$CaCO_3$. Isotopic fractionation between $CO_{2,g}$ and $CO_{2,aq}$ was not considered. Since no α coefficients were measured for aqueous complexes, e.g.$CaCO_3^o$, $CaHCO_3^+$, we assumed that such α inherit those for HCO_3^- and CO_3^{2-} ions, i.e. $\alpha_{Ca(HCO_3)+\text{-}C} \cong \alpha_{HCO_3\text{-}\text{-}C}$, $\alpha_{CaCO_3o\text{-}}$ C $\cong \alpha_{(CO_3)\text{-}2\text{-}C}$, etc. Bulk composition of the system ^{12}C-^{13}C-Ca-Cl-F-H-K-Mg-N-Na-O-S-Sr (89 species) was composed from that of a model Earth atmosphere, normative seawater of 35% salinity and H_2O. Variant AWS was set so that C isotopic composition is buffered by the atmospheric reservoir (10000 kg atmosphere of $\delta^{13}C_{CO_2} = -6.9$‰ + 1 kg of seawater). Variant WAS was specified so that C isotopes were buffered by excess calcite (1 kg seawater + 0.1M $CaCO_3$ with $\delta^{13}C_{CaCO_3} = -1.1$‰). As seen from Table 1, calculated values of $\delta^{13}C$ are quite realistic, and values of lnα agree well with experimental data (Ohmoto, 1986).

A model of equilibrium fluid-rock interaction in a hydrothermal system at P = 1 kbar and T = 250°C was constructed to test the temperature behaviour of ΔG^{oi}_{fAX} dataset for carbon isotopic compounds. In variant WR of the system Al-Ba-^{12}C-^{13}C-Ca-Cl-F-H-K-Mg-Na-O-S-Si-Sr (169 species), the bulk composition was set by H_2O/rock ratio 1:1.33, H_2 used as reductant, and C (graphite) included. Bulk rock composition was a mixture of K-feldspar, muscovite, quartz, plagioclase, pyrite, pyrrhotite, and magnetite. Bulk C isotopic composition was set by adding 1 mole of $CaCO_3$ with $\delta^{13}C = -1.1$‰. Our calculations resulted in good agreement with (Ohmoto, 1972) data (Table 2).

Conclusions

A technique for consistent extension of thermodynamic database with isotopic forms of compounds was implemented in Selektor-A code. A subset for ^{13}C and ^{12}C solid, gaseous and aqueous species, used in Gibbs minimisation calculations of equilibria at both ambient and hydrothermal conditions, provided good agreement with independent carbon isotope composition and fractionation data. Such direct isotopic equilibrium calculations provide a fulcrum for assessment of consistency of the experimental fractionation constants and for studies of isotope partition in natural systems.

References

Golyshev, S.I., Padalko, N.L., and Pechenkin, S.A. (1981) *Geokhimija*, **10**, 1427–41 (in Russian).

Grichuk, D.V. (1987) *Geokhimija* **2**, 178–91 (in Russian).

Karpov, I.K, Chudnenko, K.V. and Kulik, D.A. (1997) *Amer.J.Sci.* 297, 767-806.

Ohmoto, H. (1972) *Econ.Geol.*, **67**, 551–78.

Taylor, B.E. (1986) *Rev. Miner.*, **16**, 185–219.