A new theoretical calculation of the equilibrium constant and temperature for the carbon isotope exchange reaction between CH_4 and CO_2

Abstract

The equilibrium isotope fractionations among C-O-H gases in a variety of geological settings are commonly used as isotope geothermometers to evaluate the temperatures of geothermal fluids at depth, subsurface fluid-rock interactions, volcanic-hydrothermal systems and natural gas pools. However， due to limited experimental data and sophisticated theoretical calculations, applications of these geothermometers have been restricted. This study uses the carbon isotope exchange reaction between CH_4 and CO_2 as a case study to develop theoretical methods that can improve accuracies in calculating harmonic vibrational frequencies for CH_4 and CO_2, the equilibrium constants and temperatures for the carbon isotope exchange reaction between CH_4 and CO_2. Results suggest that the Bigeleisen-Mayer equation is sufficient to calculate the equilibrium constants and temperatures associated with the isotope exchange reaction between CH_4 and CO_2 with an accurate estimation of molecular harmonic vibrational frequencies. Calculations of the harmonic frequencies of CH_4 and CO_2 are achieved using the B3LYP density functional method with the 6-311+G(d) basis set, and the calculated harmonic frequencies are highly consistent with experimental values. The frequency correction factor is taken as 1.022 which puts the calculated fractionation factors in good agreement with experimental values. The calculated equilibrium constants are comparable to experimental data and a theoretical data set. They are highly consistent. In order to improve the accuracy and efficiency for solving equilibrium temperatures using the Bigeleisen-Mayer equation,

1

symbol operation and iterative algorithm in the MatLab software have been applied to compute the temperatures instead of using limited theoretical data sets or empirical fit equations. Our calculated results suggest that this algorithm can rapidly and conveniently yield relatively precise equilibrium temperatures. This algorithm can thus provide an important tool to evaluate whether the carbon isotope exchange reaction for CH_4 and CO_2 has attained equilibrium and estimate the formation temperature of CH_4 and CO_2 in high temperature geothermal systems.

Keywords: Isotope; Equilibrium fractionation; Temperature; New algorithm

1. **Introduction**

Stable isotope fractionation refers to mass dependent and/or mass independent effects, while the former is mainly controlled by kinetic isotope processes or equilibrium isotope effects, the latter may be associated with a photochemical process (Bigeleisen and Mayer, 1947; Clayton et al., 1973; Thiemens, 1999, 2006; Urey, 1947). The equilibrium isotope fractionations among C-O-H gases in a variety of geological settings are commonly used as isotope geothermometers to evaluate the temperatures of geothermal fluids at depth, subsurface fluid-rock interactions, volcanic-hydrothermal systems and natural gas pools (Chacko et al., 2001; Fiebig et al., 2004, 2013; Gherardi et al., 2005; Giggenbach, 1982, 1997; Schauble, 2004; Stolper et al., 2014, 2015; Wolfsberg et al., 2009). For example, the isotope

geothermometers between the pairs CO_2-CH_4, H_2O-H_2, CO_2-H_2O and H_2-CH_4 have been used

to evaluate the temperatures at depth in active geothermal systems (Arnason, 1977; Gunter

and Musgrave, 1971; Hulston, 1977; Panichi et al., 1977; Shangguan et al., 2006). However,

there still exists much debate on the relative importance of equilibrium thermodynamic and

kinetic processes in controlling the isotope compositions of geothermal gases even in high

temperature geothermal systems (Fiebig et al., 2013; Gherardi et al., 2005; Giggenbach, 1997;

Horita, 2001). This study uses the CH_4-CO_2 isotope geothermometer as a case study to further

develop a theoretical calculation of the equilibrium constant and temperature for the carbon

isotope exchange reaction between CH_4 and CO_2 in geothermal systems. Major reasons

include (1) CH_4 and CO_2 are most probably in isotope equilibrium when they are formed

together in high temperature geothermal systems (Fiebig et al., 2004, 2013; Panichi et al.,

1977; Shangguan et al., 2006); (2) The CH_4-CO_2 isotope geothermometer can be used to

estimate whether the isotope equilibrium between CH_4 and CO_2 has been reached, and if the

equilibrium fractionation is obtained, the temperatures derived from this geothermometer

could reflect the formation temperature of geothermal gases, at least the formation

temperature of CO_2 and CH_4 (Panichi et al., 1977); (3) Most isotope geothermometers are

based on a theoretical method proposed by Urey (1947) and Bigeleisen and Mayer (1947),

however, the theoretical method is not sufficient to deal with H/D isotope exchange reactions

(Liu et al., 2010; Urey, 1947). In general, the CH_4-CO_2 isotope geothermometer is a reliable

tool for evaluating the temperatures of geothermal fluids at depth and plays an important role

in geothermal exploration and risk assessment (Fiebig et al., 2013; Shangguan et al., 2006).

Based on harmonic oscillator and rigid rotator models, Urey (1947) and Bigeleisen and

Mayer (1947) proposed independently a theoretical method (e.g. Bigeleisen-Mayer equation) to estimate the equilibrium constants or temperatures for isotope exchange reactions. Since then, researchers have made corrections to the Bigeleisen-Mayer equation to improve accuracy of the theoretical evaluation of the equilibrium constants (Barone, 2005; Bigeleisen, 1996; Ellingson et al., 2007; Liu et al., 2010; Liu and Liu, 2016; Richet et al., 1977; Wolfsberg et al., 1970). However, these corrections were mainly effective with respect to isotope exchange reactions in aqueous solutions or H/D isotope exchange (Wolfsberg et al., 1970). According to the Bigeleisen-Mayer equation, one of the most interesting characteristics of equilibrium isotope fractionation is that it only depends on temperature. The most important application of this characteristic is to determine the temperatures at which geological formations were laid down (Urey, 1947). However, it has been difficult to directly calculate the temperatures according the Bigeleisen-Mayer equation or other corrected equations due to their complexities. Thus researchers usually calculate the corresponding fractionation factors at different temperature values in the first place, then work out a relationship table or further apply this data to derive fit equations (such as, $10^3\ln\alpha=a+b/T$; $10^3\ln\alpha=a+b/T+c/T^2$ and $10^3\ln\alpha=a+b/T+c/T^2+d/T^3$, etc., where a, b, c and d are constants, α and T are the equilibrium constant and temperature, respectively) to estimate the equilibrium temperatures (Bigeleisen and Mayer, 1947; Chacko et al., 2001; Horita, 2001; Richet et al., 1977; Stern et al., 1968). However, the calculated relationship data is extremely limited, and these fit equations cannot be extrapolated. They also significantly underestimate or overestimate fractionation factors or temperature values on many occasions (Horita, 2001; Richet et al., 1977).

This study uses the carbon isotope exchange reaction between CH_4 and CO_2 as a case study. It focuses on developing methods that can improve accuracies and efficiencies in calculating harmonic vibrational frequencies for CH_4 and CO_2, the equilibrium constants and equilibrium temperatures for the isotope exchange reaction between CH_4 and CO_2. In addition, implications of the calculated temperature values are discussed.

2. **Theoretical method and results**

2.1 Theoretical method for equilibrium isotope fractionation between CH_4 and CO_2

A typical carbon isotope exchange reaction for CH_4 and CO_2 can be written as

$$^{12}CO_2 + {}^{13}CH_4 \leftrightarrow {}^{13}CO_2 + {}^{12}CH_4 .$$
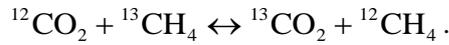
The equilibrium constant or fractionation factor $\alpha_{CO_2-CH_4}$ for this reaction is given as,

$$\alpha_{CO_2\text{-}CH_4} = \frac{R_{CO_2}}{R_{CH_4}} = \frac{1000 + \delta^{13}C_{CO_2}}{1000 + \delta^{13}C_{CH_4}} = \left(\frac{q_{^{13}CO_2}}{q_{^{12}CO_2}}\right) \Bigg/ \left(\frac{q_{^{13}CH_4}}{q_{^{12}CH_4}}\right) \tag{1}$$

where $q's$ are the reduced partition functions of these molecules.

For carbon dioxide (linear) molecule,

$$\frac{q_{^{13}CO_2}}{q_{^{12}CO_2}} = \prod_1^{3N-5} \frac{u_i^*}{u_i} \frac{e^{-u_i^*/2}\left(1 - e^{-u_i}\right)}{e^{-u_i/2}\left(1 - e^{-u_i^*}\right)} \tag{2}$$

and for methane (non-linear) molecule,

$$\frac{q_{^{13}CH_4}}{q_{^{12}CH_4}} = \prod_1^{3N-6} \frac{u_i^*}{u_i} \frac{e^{-u_i^*/2}\left(1 - e^{-u_i}\right)}{e^{-u_i/2}\left(1 - e^{-u_i^*}\right)} \tag{3}$$

where *3N-5*(6) stands for the amount of normal vibration of the *N*-atomic molecule,

5

$$u_i = \frac{hc\omega_i}{kT}, u_i^* = \frac{hc\omega_i^*}{kT},$$ h is the Planck constant, c is the speed of light, ω_i and ω_i^* are

the harmonic frequency of normal mode i for light and heavy isotopic molecule respectively,

k is the Boltzmann constant, and T is the temperature (Bigeleisen and Mayer, 1947; Urey,

1947; Wolfsberg et al., 2009).

2.2 Calculated results

2.2.1 Harmonic frequencies

Based on equations (1)-(3), fractionation factors can be calculated for given temperature

values if the molecular harmonic frequencies are known. In this study, the harmonic

frequency calculations for CH_4 and CO_2 were performed using Gaussian 09 and GaussView 5

software (Frisch et al., 2009). Gaussian 09 is based on fundamental laws of quantum

mechanics and can be used to predict molecular structures, vibrational frequencies and

energies. GaussView 5 is a graphical interface used in conjunction with Gaussian 09. It helps

the creation of Gaussian input files and the interpretation of Gaussian output. Several variants

of density functional theory (DFT) (such as B-LYP, B3-LYP, B3-P86, and B3-PW91) with the

3-21G, 6-31+G(d), 6-311G(d, p), and 6-311G(df, p) basis sets are widely used to calculate

harmonic vibrational frequencies in the Gaussian software (Frisch et al., 2009; Scott and

Radom, 1996). Of various hybrid DFT methods, the B3LYP functional has been widely used

(Andersson and Uvdal, 2005; Scott and Radom, 1996). Therefore, this study used the B3LYP

method combined with the 6-311+G(d) basis set for the calculations of geometry

optimizations and harmonic vibrational frequencies.

The theoretical harmonic frequencies calculated for CH_4 and CO_2 molecules, such as $^{12}CH_4$, $^{13}CH_4$, $^{12}CO_2$ and $^{13}CO_2$, are given in Table 1. These values are compared with the experimental data from previous studies (Gray and Robiette, 1979; Lee et al., 1995; Pariseau et al., 1965) to check the accuracy of the calculation. In Table 1, the $\Delta_\omega (\omega_2-\omega_3)$ values for CH_4 are between -4.75 cm^{-1} and 21.79 cm^{-1}, the $\Delta_\omega (\omega_1-\omega_3)$ values for CO_2 are between -23.94 cm^{-1} and 4.54 cm^{-1}. Fig .1 shows that the calculated and experimental values plot along a line with the slope of ~1.00 and intercept of ~0.00. This reflects that the calculated harmonic vibrational frequencies are in close agreement with experimental values for these molecules ($^{12}CH_4$, $^{13}CH_4$, $^{12}CO_2$ and $^{13}CO_2$), although minor differences still exist (Table 1, Fig. 1).

Table 1

Calculated theoretical harmonic frequencies, experimental values and multiplicity of degenerate frequencies.
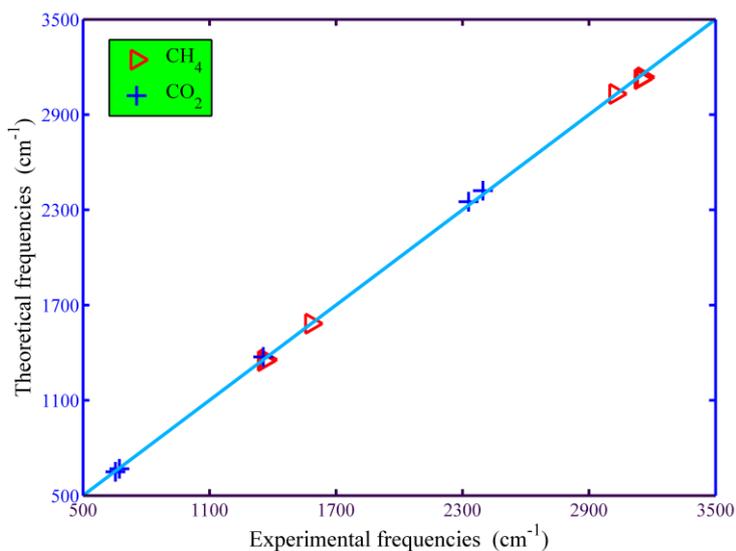
Fig. 1. Theoretical harmonic vibrational frequencies versus experimental frequencies of methane and carbon dioxide. The experimental frequencies of methane are harmonic, while the frequencies of carbon dioxide are from a direct experimental observation (the frequency data are all from Table 1).

2.2.2 Equilibrium constants

In this study the calculated harmonic vibrational frequencies for CH_4 and CO_2 have been corrected and the correction factor is taken to be 1.022 which makes the calculated equilibrium constants close to the experimental values provided by Horita (2001). Table 2 lists the calculated equilibrium constants, experiment values and errors. The results show that the error range of β_1-β_2 is between -0.3223 and 0.4948. Fig. 2 compares the calculated equilibrium constants with the experimental values by Horita (2001). Table 3 and Fig. 3 compare the equilibrium constants calculated in this study with the data sets calculated by Richet et al. (1977). Table 3 shows the error range of γ_1-γ_2 is from -0.0022 to -0.0002. We find that the equilibrium constants calculated in this study using the correction factor are in good agreement with experimental and calculated results from previous studies.

Table 2

Calculated fractionation factors (expressed in $10^3 ln\alpha_{CO_2-CH_4}$) between 200.6°C and 550.0°C in this study and experimental values from Horita (2001).

Table 3

Isotope fractionation factors (expressed as $ln\alpha_{CO_2-CH_4}$) calculated in this study (γ_2) between 0°C and 1300°C and calculated by Richet et al. (1977) (γ_1).
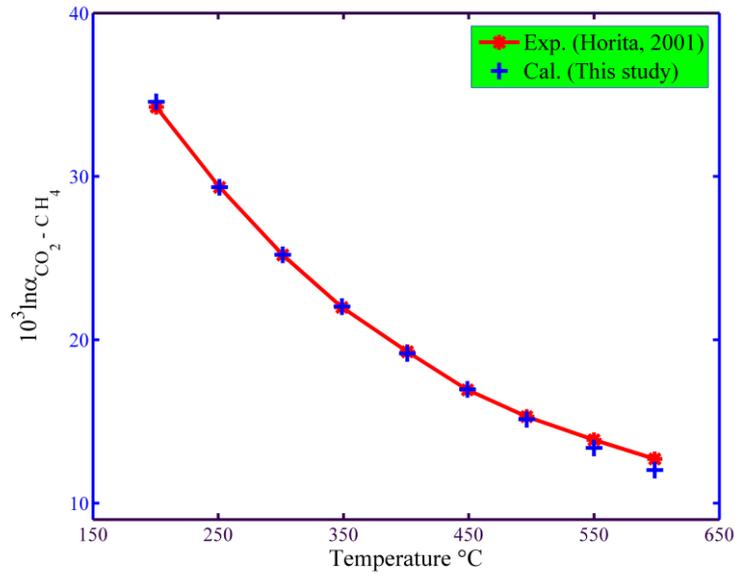
Fig. 2. Plot of the calculated equilibrium constants in this study (expressed as $10^3\ln\alpha_{CO_2\text{-}CH_4}$) between 200°C and 600°C versus experimental values by Horita (2001).
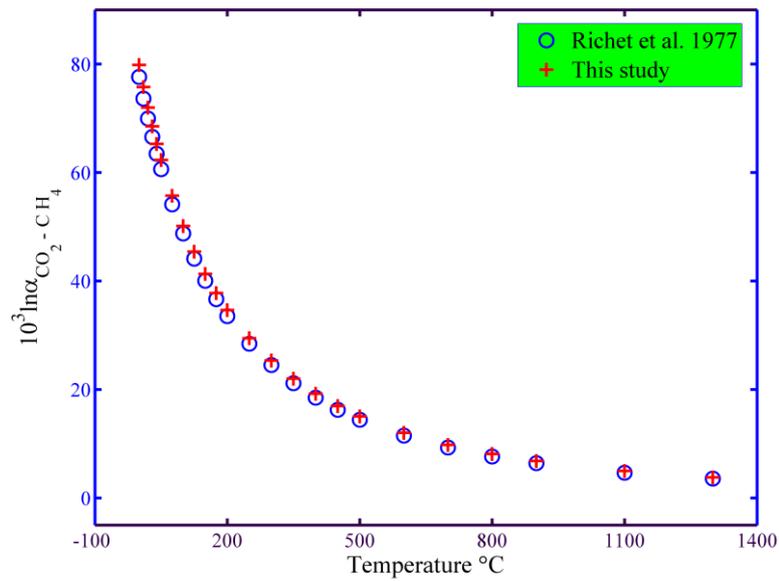
Fig. 3. Plot of calculated equilibrium constants in this study (expressed as $10^3\ln\alpha_{CO_2\text{-}CH_4}$) from 0°C to 1300°C versus calculated values by Richet et al. (1977).

2.2.3 Equilibrium temperatures

Equilibrium temperatures are calculated directly according to equation (1) instead of using limited data sets or empirical fit equations. The symbol operation and iterative algorithm in the MatLab software are applied for calculations (Supplementary Information). The algorithm (source program) is easy to operate. The only input data is the fractionation factor $\alpha_{CO_2\text{-}CH_4}$, and then the corresponding equilibrium temperature can be calculated within one minute. Table 4 shows an exact set of temperature values, the corresponding fractionation factors, and the calculated temperature values. The results show that absolute errors associated with temperature values are less than 2°C.

Table 4

Comparison of calculated temperatures and exact values for different fractionation factors.

3. **Discussion**

In the Bigeleisen-Mayer equation, molecular vibrational frequencies should be pure harmonic frequencies, and they can be obtained either theoretically or via experiments. In general, it is not easy to obtain pure harmonic frequencies from experimental spectroscopic data, particularly for polyatomic molecules and isotopically substituted molecules (Liu et al., 2010). However, the DFT methods can be used easily to calculate pure harmonic frequencies (Andersson and Uvdal, 2005; Scott and Radom, 1996). In this study, we use the B3LYP functional method with the 6-311+G(d) basis set to calculate vibrational frequencies for CH_4 and CO_2. The calculated frequencies are comparable to the experimental observed and harmonic ones (Table 1, Fig. 1). Our calculated results are highly consistent with

experimental values, especially for $^{12}CH_4$ and $^{13}CH_4$. This agreement suggests that the B3LYP

method with the 6-311+G(d) basis set is very reliable and can be used to precisely estimate

the harmonic frequencies for some molecules and their isotopocules.

Our calculated equilibrium constants (Table 2, Table 3, Fig. 2 and Fig. 3) are in good

agreement with experimental and calculated values from previous studies (Horita, 2001;

Richet et al., 1977), suggesting that applying the Bigeleisen-Mayer equation can achieve

relatively precise equilibrium constants if molecular harmonic frequencies are estimated with

high accuracy. Table 2 and Fig. 2 compare the calculated equilibrium constants with the

experimental results (Horita, 2001), the results indicate that our calculated equilibrium

constants are very accurate. Table 3 and Fig. 3 compare the equilibrium constants calculated

in this study with the presumably more accurate data sets (Richet et al., 1977) which were

attained from a complicated corrected Bigeleisen-Mayer equation, the results suggest that two

different methods can yield highly consistent fractionation factors and the higher the

temperature, the better consistency it can achieve. Therefore, under the condition that

fractionation factor $\alpha_{CO_2-CH_4}$ is given, the relatively simple equation (1) can be used to compute

the equilibrium temperature precisely.

To improve the accuracy and efficiency of solving equations to obtain equilibrium

temperatures using equation (1), the symbol operation and iterative algorithm in the MatLab

software are applied to compute the temperature values instead of using limited data sets or

empirical fit equations. This algorithm can be used to calculate the corresponding equilibrium

temperature if the input fractionation factor is between 1.08309 and 1.00086 (Table 4). In

other words, the equilibrium temperatures should be in the range between 0°C and 3000°C for

the CH_4-CO_2 isotope geothermometer. The set absolute errors associated with temperature calculations are less than 2°C. Although small differences still exist (< 2°C) between the calculated values and the exact solutions, our results suggest that they are generally in good agreement (Table 4). If it is necessary, the differences can be reduced by resetting the error range. In principle, by resetting the range of the temperature values, this algorithm can be applied to calculate any corresponding equilibrium temperature under any condition that the fractionation factor is given.

Based on the discussion above, we find that the harmonic frequencies and equilibrium constants calculated in this study are reliable and accurate by comparison with experimental and theoretical data from previous studies. This suggests that the relatively simple equation (1) compared with the theoretical method provided by Richet et al. (1977) is more suitable for dealing with equilibrium carbon isotope fractionation between CH_4 and CO_2. Furthermore, it has been difficult to calculate the equilibrium temperatures by directly applying the Bigeleisen-Mayer equation or the theoretical method provided by Richet et al. (1977), our algorithm can solve this problem very well, and can conveniently and rapidly calculate relatively precise equilibrium temperatures using the Bigeleisen-Mayer equation.

4. **Implications**

Investigations on the isotope composition of carbon dioxide and methane from geothermal fluids, hot springs, coal seams and shale rocks have been carried out for many years. However, there has been an ongoing debate on the relative importance of kinetics and equilibrium in

controlling their isotope distribution (Fiebig et al., 2004, 2013; Gherardi et al., 2005;

Giggenbach, 1997; Panichi et al., 1977; Stolper et al., 2014, 2015; Tao et al., 2007, 2015).

Our algorithm (source program) is an important tool in evaluating whether the carbon isotope

exchange reaction for CH_4 and CO_2 has attained equilibrium. Because our algorithm can

conveniently and rapidly calculate relatively precise corresponding equilibrium temperature

under the condition that fractionation factor $\alpha_{CO2-CH4}$ is known. The "equilibrium" temperature

associated with other geothermal parameters can then be used to estimate whether the isotope

equilibrium between CH_4 and CO_2 has been reached.

The formation temperatures of CH_4 and CO_2 are very important in geothermal

exploration and risk assessment. However, they are often poorly constrained in nature (Fiebig

et al., 2013; Panichi et al., 1977; Stolper et al., 2014). Some researchers have assumed that

CH_4 and CO_2 were most probably in isotope equilibrium when they were formed together in

active high temperature geothermal systems (Fiebig et al., 2013; Gherardi et al., 2005; Panichi

et al., 1977; Shangguan et al., 2006). For example, Panichi et al. (1977) applied the CH_4-CO_2

isotope geothermometer to study the formation temperature of geothermal gases in the

Larderello geothermal field. They suggested that temperatures derived from the isotope

geothermometer reflected the formation temperature of CO_2 and CH_4 and that the

temperatures actually existed in the geothermal fields. If this hypothesis on isotope

equilibrium fractionation was correct, and CO_2 and/or CH_4 from other sources were not added,

the formation temperatures of CO_2 and CH_4 could be calculated accurately by applying our

algorithm. Furthermore, the depth where they were formed together could be estimated.

Conclusions

The harmonic frequency calculations for CH_4 and CO_2 were performed using Gaussian 09 and GaussView 5, and the theoretical method was chosen as the B3LYP density functional method with the 6-311+G(d) basis set. The calculated frequencies are in close agreement with experimental values for the molecules $^{12}CH_4$, $^{13}CH_4$, $^{12}CO_2$ and $^{13}CO_2$. The frequency correction factor is taken to be 1.022 which makes the calculated fractionation factors closely approach experimental values provided by Horita (2001). Equilibrium constants are calculated for the isotope exchange reaction between CH_4 and CO_2 using equation (1). And the calculated equilibrium constants are in good agreement with the experimental values (Horita, 2001) and the theoretically calculated data sets (Richet et al., 1977). The results suggest that the equation (1) is more suitable for dealing with equilibrium carbon isotope fractionation between CH_4 and CO_2. In order to improve the accuracy and efficiency of solving for equilibrium temperatures using equation (1), a new algorithm (e.g. symbol operation and iterative algorithm in the MatLab software) is used to compute the temperatures according to equation (1) instead of using limited experimental and calculated data sets or empirical fit equations. In this algorithm, the set temperature ranges between 0°C and 3000°C, and the set absolute error is less than 2°C. The new algorithm (source program) has wide applications in geothermal exploration and associated risk assessment.

Acknowledgements

Supplementary Information

The source program applied to compute the equilibrium temperature is provided in the Supporting file.

References

Andersson, M.P., Uvdal, P., 2005. New scale factors for harmonic vibrational frequencies using the B3LYP density functional method with the triple-ζ basis set 6-311+G(d, p). J. Phys. Chem. 109, 2937-2941.

Arnason, B., 1977. The hydrogen-water isotope thermometer applied to geothermal areas in Iceland. Geothermics 5, 75-80.

Barone, V., 2005. Anharmonic vibrational properties by a fully automated second-order perturbative approach. J. Chem. Phys. 122, 014108.

Bigeleisen, J., 1996. Nuclear size and shape effects in chemical reactions. Isotope chemistry of the heavy elements. J. Am. Chem. Soc. 118, 3676-3680.

Bigeleisen, J., Mayer, M.G., 1947. Calculation of equilibrium constants for isotopic exchange reactions. J. Chem. Phys. 15, 261-267.

Chacko T., Cole, D.R., Horita, J., 2001. Equilibrium Oxygen, Hydrogen and Carbon Isotope Fractionation Factors Applicable to Geologic Systems. Rev. Mineral. Geochemistry 43, 1-81.

Clayton, R. N., Grossman, L., Mayeda, T. K., 1973. A component of primitive nuclear composition in carbonaceous meteorites. Science 182, 485-488.

Ellingson, B.A., Pu, J., Lin, H., Zhao, Y., Truhlar, D.G., 2007. Multicoefficient Gaussian-3 calculation of the rate constant for the OH+ CH_4 reaction and its $^{12}C/^{13}C$ kinetic isotope effect with emphasis on the effects of coordinate system and torsional treatment. J. Phys. Chem. A 111, 11706-11717.

Fiebig, J., Chiodini, G., Caliro, S., Rizzo, A., Spangenberg, J., Hunziker, J.C., 2004. Chemical and isotopic equilibrium between CO_2 and CH_4 in fumarolic gas discharges: generation of CH_4 in arc magmatic-hydrothermal systems. Geochim. Cosmochim. Acta 68, 2321-2334.

Fiebig, J., Tassi, F., D'Alessandro, W., Vaselli, O., Woodland, A.B., 2013. Carbon-bearing gas geothermometers for volcanic-hydrothermal systems. Chem. Geol. 351, 66-75.

Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Scalmani, G., Barone, V., Mennucci, B., Petersson, G.A., Gaussian 09, revision A.02; Gaussian Inc.: Wallingford CT, 2009.

Gherardi, F., Panichi, C., Gonfiantini, R., Magro, G., Scandiffio, G., 2005. Isotope systematics of C-bearing gas compounds in the geothermal fluids of Larderello, Italy. Geothermics 34, 442-470.

Giggenbach, W. F., 1982. Carbon-13 exchange between CO_2 and CH_4 under geothermal conditions. Geochim. Cosmochim. Acta 46 159-165.

Giggenbach W. F., 1997. Relative importance of thermodynamic and kinetic processes in governing the chemical and isotopic composition of carbon gases in high-heatflow sedimentary basins. Geochim. Cosmochim. Acta 61, 3763-3785.

Gray, D.L., Robiette, A.G., 1979. The anharmonic force field and equilibrium structure of methane. Mol. Phys. 37, 1901-1920.

Gunter, B.D., Musgrave, B.C., 1971. New evidence on the origin of methane in hydrothermal gases. Geochim. Cosmochim. Acta 35, 113-118.

Horita, J., 2001. Carbon isotope exchange in the system CO_2-CH_4 at elevated temperatures. Geochim. Cosmochim. Acta 65, 1907-1919.

Hulston, J.R., 1977. Isotope work applied to geothermal systems at the Institute of Nuclear Sciences, New Zealand. Geothermics 5, 89-96.

Lee, T.J., Martin, J.M.L., Taylor, P.R., 1995. An accurate ab initio quartic force field and vibrational frequencies for CH_4 and isotopomers. J. Chem. Phys. 102, 254-261.

Liu, Q., Liu, Y., 2016. Clumped-isotope signatures at equilibrium of CH_4, NH_3, H_2O, H_2S and SO_2. Geochim. Cosmochim. Acta 175, 252-270.

Liu, Q., Tossell, J. A., Liu, Y., 2010. On the proper use of the Bigeleisen–Mayer equation and corrections to it in the calculation of isotopic fractionation equilibrium constants. Geochim. Cosmochim. Acta 74, 6965-6983.

Panichi, C., Ferrara, G.C., Gonfiantini, R., 1977. Isotope geothermometry in the Larderello geothermal field. Geothermics 5, 81-88.

Pariseau, M.A., Suzuki, I., Overend, J., 1965. Least-Squares Adjustment of Anharmonic Potential Constants: Application to $^{12}CO_2$ and $^{13}CO_2$. J. Chem. Phys. 42, 2335-2344.

Richet, P., Bottinga, Y., Janoy, M., 1977. A review of hydrogen, carbon, nitrogen, oxygen, sulphur and chlorine stable isotope enrichment among gaseous molecules. Ann. Rev. Earth Planet. Sci. 5, 65-110.

Schauble, E.A., 2004. Applying stable isotope fractionation theory to new systems. Rev. Mineral. Geochemistry 55, 65-111.

Scott, A.P., Radom, L., 1996. Harmonic Vibrational Frequencies: An Evaluation of Hartree-Fock, Møller-Plesset, Quadratic Configuration Interaction, Density Functional Theory, and Semiempirical Scale Factors. J. Phys. Chem. 100, 16502-16513.

Shangguan, Z., Zhao, C., Gao, L., 2006. Carbon isotopic compositions of the methane derived from magma at the active volcanic regions in China. Acta. Petrol Sin. 22, 1458-1446 (in Chinese).

Stern, M.J., Spindel, W., Monse, E.U., 1968. Temperature dependences of isotope effects. J. Chem. Phys. 48, 2908-2919.

Stolper, D.A., Lawson, M., Davis, C.L., Ferreira, A.A., Neto, E.S., Ellis, G.S., Sessions, A.L., 2014. Formation temperatures of thermogenic and biogenic methane. Science 344, 1500-1503.

Stolper, D.A., Martini, A.M., Clog, M., Douglas, P.M., Shusta, S.S., Valentine, D.L., Eiler, J.M., 2015. Distinguishing and understanding thermogenic and biogenic sources of methane using multiply substituted isotopologues. Geochim. Cosmochim. Acta 161, 219-247.

Tao, M., Ma, Y., Li, Z., Li, J., Liu, P., Wang, Y., Chen, X., Zhang, A., 2015. The Isotopic Tracer and Resource Value of Microbial Gas Production in Coalbeds-A Case Study of Coalbed Gas in Enhong, China. Energy & Fuels 29, 2134-2142.

Tao, M., Shi, B., Li, J., Wang, W., Li, X., Gao, B., 2007. Secondary biological coalbed gas in the Xinji area, Anhui province, China: evidence from the geochemical features and secondary changes. Int. J. Coal Geol. 71, 358-70.

Thiemens, M.H., 1999. Mass-independent isotope effects in planetary atmospheres and the early solar system. Science 283, 341-345.

Thiemens, M. H., 2006. History and Applications of Mass-Independent Isotope Effects. Earth Planet. Sci. 34, 217-262.

Urey, H.C., 1947. The thermodynamic properties of isotopic substances. J. Chem. Soc. (Lond.), 562-581.

Wolfsberg, M., Massa, A.A., Pyper, J.W., 1970. Effect of Vibrational Anharmonicity on the Isotopic Self-Exchange Equilibria $H_2X + D_2X = 2HDX$. J. Chem. Phys. 53, 3138-3146.

Wolfsberg, M., Van Hook, W.A., Paneth, P., Rebelo, L.P.N., 2009. Isotope Effects: in the chemical, geological, and bio sciences. Springer Science & Business Media, New York.

Tables

Table 1

Calculated theoretical harmonic frequencies, experimental values and multiplicity of degenerate frequencies.

	Experimental[a]		Theoretical	Difference[b]	Degeneracy
	Observed ω_1	Harmonic ω_2	Harmonic ω_3	Δ_ω	
$^{12}CH_4$	2916.5	3025.5	3030.25	-4.75	1
	1533.3	1582.7	1582.64	0.06	2
	3019.2	3156.8	3135.06	21.74	3
	1310.8	1367.4	1355.13	12.27	3
$^{13}CH_4$	2915.4	3025.5	3030.25	-4.75	1
	--	1582.7	1582.64	0.06	2
	3009.5	3145.6	3123.81	21.79	3
	1302.8	1358.9	1346.75	12.15	3
$^{12}CO_2$	1354.91	--	1373.18	-18.27	1
	673.00	--	668.46	4.54	2
	2396.49	--	2420.43	-23.94	1
$^{13}CO_2$	1354.91	--	1373.18	-18.27	1
	653.83	--	649.44	4.39	2
	2328.22	--	2351.54	-23.32	1

[a] Experimental vibrational frequencies for methane are from Lee et al. (1995) and Gray and Robiette (1979); for carbon dioxide are from Pariseau et al. (1965).

Table 2

Calculated fractionation factors (expressed in $10^3\ln\alpha_{CO2-CH4}$) between 200.6°C and 550.0°C in this study and experimental values from Horita (2001).

Temperature (°C)	$10^3\ln\alpha_{CO2-CH4}$		Error $\beta_1-\beta_2$
	Experimental values β_1	Calculated values β_2	
200.6000	34.2400	34.5623	-0.3223
251.1000	29.3300	29.3412	-0.0112
301.5000	25.1900	25.2008	-0.0108
348.8000	21.9800	22.0370	-0.0570
401.0000	19.2600	19.1629	0.0971
449.0000	16.9300	16.9664	-0.0364
496.3000	15.2900	15.1341	0.1559
550.0000	13.8700	13.3752	0.4948

Table 3

Isotope fractionation factors (expressed as $\ln\alpha_{CO2-CH4}$) calculated in this study (γ_2) between 0°C and 1300°C and calculated by Richet et al. (1977) (γ_1).

Temperature (°C)	$\ln\alpha_{CO2-CH4}$		Error $\gamma_1-\gamma_2$
	γ_1	γ_2	
0	0.0776	0.0798	-0.0022
10	0.0736	0.0757	-0.0021
20	0.0700	0.0720	-0.0020
30	0.0666	0.0685	-0.0019
40	0.0634	0.0653	-0.0019
50	0.0606	0.0623	-0.0017
75	0.0541	0.0557	-0.0016
100	0.0488	0.0501	-0.0013
150	0.0400	0.0413	-0.0013
200	0.0335	0.0346	-0.0011
250	0.0284	0.0294	-0.0010
300	0.0245	0.0253	-0.0008
350	0.0211	0.0219	-0.0008
400	0.0185	0.0192	-0.0007
450	0.0163	0.0169	-0.0006
500	0.0144	0.0150	-0.0006
600	0.0115	0.0120	-0.0005
700	0.0093	0.0098	-0.0005
800	0.0076	0.0081	-0.0005
1100	0.0046	0.0050	-0.0004

1300	0.0036	0.0038	-0.0002

Table 4

Comparison of calculated temperatures and exact values for different fractionation factors.

$\alpha_{CO2-CH4}$	Temperature (°C)	
	Exact values[c]	Calculated values
1.0831	0	0
1.0573	75.0	75
1.0421	150.6	150
1.0256	300.9	300
1.0151	500.5	500
1.0098	700.7	701
1.0068	900.4	901
1.00298	1500.6	1501
1.001803	2000.8	2001
1.000865	2999.3	2999

[c] The exact value is a given value that is used to calculate the corresponding fractionation factor according to equation (1).