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Thermodynamic model and properties for the Au-Bi melt under hydrothermal conditions

Introduction

Few readily available computer packages are able to combine non-ideal melts with complex electrolyte solutions, reflecting the current paradigm that "melts and hydrothermal fluids don't mix". One exception is the *H*ydro*Ch*emistry code (HCh; Shvarov and Bastrakov, 1999), which enables calculation of equilibria among minerals (including solid solutions), melts or non-electrolyte solutions (ideal or Non-Random Two-Liquid solution model; NRTL; Renon, 1968), electrolyte solutions, and gases (ideal or non-ideal).

The Au-Bi binary system contains three minerals (bismuth, gold, and maldonite; Au_2Bi - e.g. Chevalier, 1988; Okamoto and Massalski, 1983). We describe hereafter how we performed a new evaluation to obtain a self-consistent model in HCh. The HCh model appropriately reproduces the important features of the phase diagram over the range 25˚C to 450˚C (Fig. DR1, Table DR1).

Figure DR1. Topology of the Au-Bi binary phase diagram (at 1 bar), calculated using the model developed in HCh. The experimental data from Nathans and Leider (1962) are shown as circles.

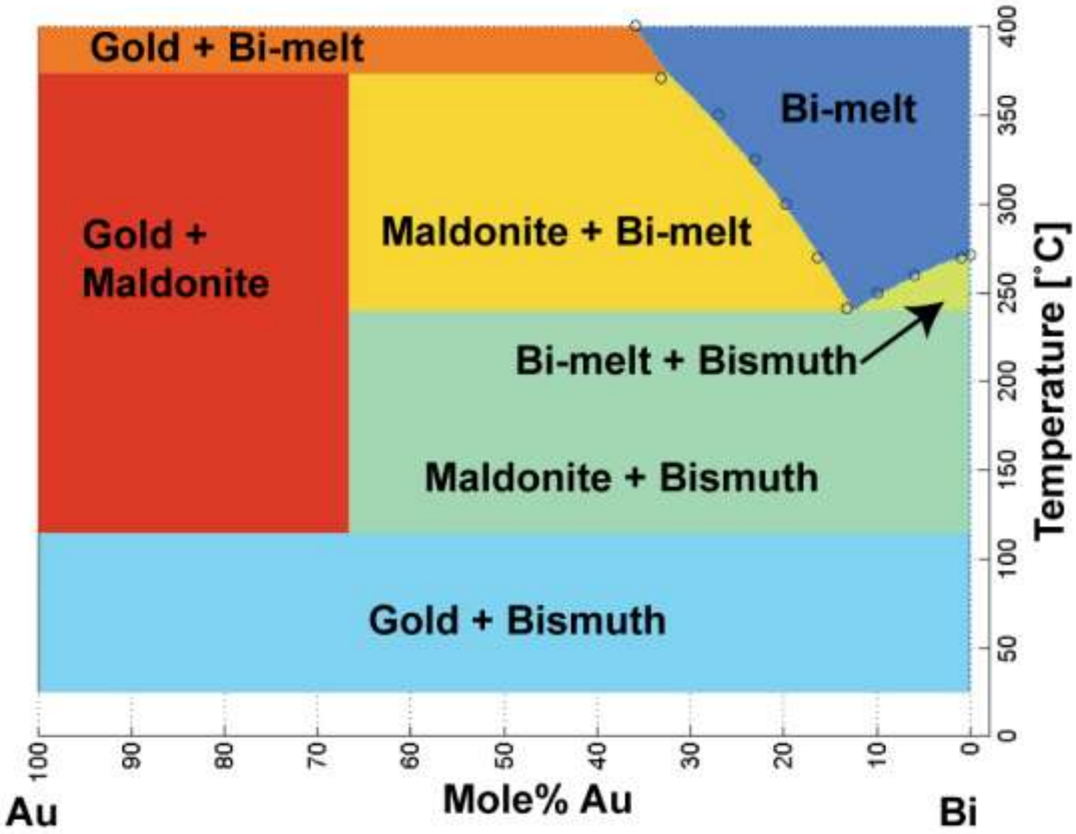

Table DR1. Experimental and calculated values for points of interest in the Au-Bi binary phase diagram.

	HCh model	Other Calc. and Exptl. Values	References
Bi melting	271.37˚C	271.37˚C	Okamoto and Massalski (1983)
Au melting	1064.4˚C	1064.4˚C	Okamoto and Massalski (1983)
Eutectic	240.1˚C, x_{Bi} = 0.875	241.25˚C, x_{Bi} ~ 0.86	Vogel (1906)
		240˚C, x_{Bi} = 0.8236	Hajicek (1948)
		241.10˚C, x_{Bi} = 0.868(3)	Nathan and Leider (1996)
		241˚C, x_{Bi} = 0.85	Gather and Blachnik (1975)
		240.8(4)˚C, x_{Bi} = 0.864(2)	Evans and Prince (1983)
Peritectic	373.3˚C, x_{Bi} = 0.676	371˚C, x_{Bi} = 0.669(3)	Nathan and Leider (1996)
		373, x_{Bi} = 0.68	Gather and Blachnik (1975)
		378, x_{Bi} = 0.666(3)	Evans and Prince (1983)
		373, x_{Bi} not reported	Jurriaanse (1935)
Au_2Bi(s) = 2Au(s) + Bi(s)	114.3˚C	~116˚C	Okamoto and Massalski (1983)

The HCh model

The HydroChemistry package (HCh) solves equilibria among pure minerals, solid solutions, aqueous fluids, melts and gases using the Gibbs Free Energy Minimization method (Shvarov and Bastrakov, 1999). Consequently, the Gibbs Free Energy of each phase and aqueous species in the system must be available over the P-T range of interest.

The following standard state conventions apply in HCh (Shvarov and Bastrakov, 1999):

- Stoichiometric minerals or pure liquids/melts (including water): unit activity of the pure component at all temperatures and pressures.
- Gases (including stable and metastable steam): the hypothetical state of unit fugacity (1 bar) at any temperature.
- Aqueous species (other than H_2O): unit activity of the species in a hypothetical 1 molal solution referenced to infinite dilution at any temperature and pressure.

The model and thermodynamic properties for Bi minerals, melt and aqueous species developed in HCh was transferred to the Geochemist's Workbench (Bethke, 1996), to draw activity-activity diagrams. This was accomplished using the UT2K and K2GWB utilities, and changing the P-T grid in GWB as outlined by Cleverley and Bastrakov (2005). GWB calculates equilibrium among pure minerals, aqueous solutions and gases by solving a system of mass balance and mass action equations, and does not allow consideration of non-ideal melts of mixed composition or solid solutions, therefore it is useful for descriptions of speciation trends but HCh is required for modelling reactions involving the Bi (+/- Au) melt.

Gibbs free energy for pure melts & minerals:

The Gibbs free energy of formation from the elements ($\Delta_f G^0(T,P)$) of minerals and melts at any pressure and temperature (T, P) is calculated relative to the Gibbs free energy of formation at the reference conditions, $T_r = 25^\circ C$, $P_r = 1$ bar, using the following equation:

$$\Delta_f G^0(T,P) = \Delta_f G^0(T_r,P_r) - S^0(T_r,P_r)\cdot(T - T_r) + \int_{T_r}^{T} Cp(t)\,dt - T\cdot\int_{T_r}^{T}\frac{Cp(t)}{t}dt + \int_{P_r}^{P} V(T,p)\,dP\,, \qquad (1)$$

where $S^0(T_r)$, $V(T_r)$ and $\Delta_f G^0$ are the standard molal entropy, volume and Gibbs free energy of formation, and *Cp(t)* is the molal isobaric heat capacity of the mineral at 1 bar, defined as a power function.

The properties for Au(s), Bi(s), Au(l) and Bi(l) are regressed from the data listed in Barin (1989; Table DR2). For maldonite, the heat capacity (c_p) expression determined by Wallbrecht et al. (1981) was used, and the standard molal entropy and Gibbs free energy of formation for this mineral were adjusted in order to reflect the breakdown of maldonite into Au(s) + Bi(s) below around ~389 K and the peritectic at ~374˚C (Table DR1).

Table DR2. Thermodynamic properties for minerals and pure melts in the HCh model for the Au-Bi binary.

Phase	Gold(s)	Gold(l)	Bismuth(s)	Bismuth(l)	Maldonite
$\Delta_f G^0_{P_r,T_r}$ [J/mole]	0	32317	0	8141	4878
$S^0_{P_r,T_r}$ [J/mole*K]	47.497	73.270	56.735	86.670	213.199
$V^0_{P_r,T_r}$ [J/bar]	1.0215	0.900	2.131	2.060	3.840
Cp expression [J/mol/K]	$128.143 - 7.714547\ 10^{-2}\ T + 1530557\ T^{-2} - 1721.841\ T^{-0.5} + 3.041287\ 10^{-5}\ T^{2}$	30.962	$11.854 + 3.06\ 10^{-2}\ T + 410183.5\ T^{-2}$	$-25.797 + 3.00\ 10^{-2}\ T + 0.8976\ T^{-2} + 985.9979\ T^{-0.5} - 7.90\ 10^{-6}\ T^{2}$	$24.5 + 6.25\ 10^{-3}\ T - 3.0105\ 10^{4}\ T^{-2}$
Reference	Barin (1989)	Barin (1989)	Barin (1989)	Barin (1989)	Cp from Wallbrecht et al. (1981); $\Delta_f G^0_{P_r,T_r}$ and $S^0_{P_r,T_r}$ this study.

The chosen properties for the minerals bismuthinite and bismite are listed in Table DR3. The entropy of and free energy of bismuthinite were taken from Barin, 1989. There is a large uncertainty about the heat capacity and enthalpy of bismuthinite, with different values being reported by Mills (1974) and Pankratz et al. (1987). Barin (1989) choose enthalpy and entropy values similar to those in Mills (1974), but the heat capacity expression given by Pankratz et al. (1987). We chose to retain Mills (1974) heat capacity values, because the values proposed by Pankratz et al. (1987) result in the prediction of extremely high stability of bismuthinite versus native bismuth or bismuth melt over the conditions of interest in the present study.

Such a high stability is not consistent with the observation of native bismuth as a common mineral in many ore deposits.

Table DR3. Thermodynamic properties for bismuthinite and bismite.

Phase	Bismuthinite	Bismite
$\Delta_f G^0_{P_r,T_r}$ [J/mole]	-140347	-485912
$S^0_{P_r,T_r}$ [J/mole*K]	200.40	116.461
$V^0_{P_r,T_r}$ [J/bar]	7.552	4.973
Cp expression [J/mol/K]	114.5508+ $2.7717\ 10^{-2}$ T	103.5122+ $3.3472\ 10^{-2}$ T

The model also includes the mineral bismite (Bi_2O_3). This mineral is known mainly as a weathering product of Bi-rich ores, but does not form under conditions typical of most hydrothermal ore deposits. Bismite is added for completeness and for allowing comparison with the α-Bi_2O_3 solubility experiments of Kolonin and Laptev (1982). The heat capacity (Table DR3) is taken from Naumov et al. (1974). The Gibbs free energy and entropy listed by Naumov et al. (1974) were adjusted to reproduce the solubility data from Kolonin and Laptev (1982) (Log K1 in Table DR4): $\Delta_f G^0_{P_r,T_r}$ was adjusted from -493.712 kJ/mole to -485.912 kJ/mole, and $S^0_{P_r,T_r}$ from 151.46 J/mole/K to 116.461 J/mole/K. The molar volume data for all solids are from Robie and Hemingway (1995).

Au-Bi Melt

The non-ideality of the Au-Bi melt was described using the non-random two-liquid solution model implemented in HCh (NRTL; Renon, 1968). The chemical potential of the melt, $\mu^0_{melt,NRTL}$, is described by the following expression:

$$\mu^0_{melt,NRTL} = x_{Bi(l)}\left(\mu^0_{Bi(l)} + RT(\ln\gamma_{Bi(l)} + \ln x_{Bi(l)})\right) + x_{Au(l)}\left(\mu^0_{Au(l)} + RT(\ln\gamma_{Au(l)} + \ln x_{Au(l)})\right) \quad (2)$$

where $\mu^0_{Au(l)}$ and $\mu^0_{Bi(l)}$ are the molal chemical potential for the pure melts, $x_{Au(l)}$ and $x_{Bi(l)}$ are the mole fractions of Au and Bi in the melt, respectively, and $\gamma_{Au(l)}$ and $\gamma_{Bi(l)}$ are the activity coefficients for Au and Bi in the melt.

The NRTL model describes the non-ideality of the Au-Bi melt using three empirical parameters, α_{12}, τ_{12}, τ_{21}; index 1 corresponds to Bi(l), and 2 to Au(l). The NRTL equations are as follow:

$$G_{12} = \exp(-\alpha_{12}\tau_{12}) \quad (3)$$

$$G_{21} = \exp(-\alpha_{12}\tau_{21}) \quad (4)$$

$$\alpha_{12} = \alpha_{21} \quad (5)$$

$$\ln(\gamma_{Bi(l)}) = x^2_{Au(l)}\left(\frac{\tau_{21}G^2_{21}}{(x_{Bi(l)} + x_{Au(l)}G_{21})^2} + \frac{\tau_{12}G_{12}}{(x_{Au(l)} + x_{Bi(l)}G_{12})^2}\right) \quad (6)$$

and $$\ln(\gamma_{Au(l)}) = x^2_{Bi(l)}\left(\frac{\tau_{12}G^2_{12}}{(x_{Au(l)} + x_{Bi(l)}G_{12})^2} + \frac{\tau_{21}G_{21}}{(x_{Bi(l)} + x_{Au(l)}G_{21})^2}\right) \quad (7)$$

Non-linear least-square fitting was used to optimise the NRTL parameters in order to reproduce the data of Nathans and Leider (1962) concerning the composition of the liquidus. As noted by Okamoto and Massalski (1983), the Nathans and Leider (1962) data is preferred over those of Vogel (1906) because the presence of the Au_2Bi intermediate was not observed in the latter study, and the melting point of bismuth was reported about 5˚C lower than the accepted value. The resulting NRTL parameters are:

$$\alpha_{12} = 0.5547\ ,\ \tau_{12} = -2.7352\ ,\ \tau_{21} = -1.6006 \qquad (8)$$

Aqueous species for bismuth and gold

In HCh, properties for aqueous species can be introduced using the revised Helgeson-Kirkham-Flowers equations of state (HKF) (Shock et al., 1992; Tanger and Helgeson, 1988). Alternatively, the Gibbs free energies of aqueous complexes can be calculated according to the modified Ryzhenko-Bryzgalin model (MRB) (Borisov and Shvarov, 1992) from their $pK_{diss}(T,P)$ values:

$$\Delta G(T,P) = \sum n_i \cdot \Delta G_i(T,P) - R \cdot T \cdot \ln(10) \cdot pK_{diss}(T,P), \qquad (9)$$

where $\Delta G_i(T,P)$ are Gibbs free energies of "basic" species described using the HKF model, and n_i are stoichiometric coefficients. The temperature and pressure dependence of $pK_{diss}(T,P)$ values is represented by the equation:

$$pK_{diss}(T,P) = \frac{T_r}{T} \cdot pK_{diss}(T_r,P_r) + B(T,P) \cdot (zz/a)_{eff}, \quad (10)$$

where $(zz/a)_{eff}$ is the effective property of the complex which depends on temperature:

$$(zz/a)_{eff} = A + \frac{B}{T}. \quad (11)$$

The parameter B(T,P) does not depend on the complex type and is computed from the dissociation constant of water according to Marshall and Franck (1981). For H_2O $(zz/a)_{eff}$ = 1.0107.

The aqueous speciation model for bismuth and gold was built into the HCh framework using broadly the same principles as those used by Skirrow and Walshe (2002) in their study of the Tennant Creek deposits. The properties for most Bi aqueous species are derived from the experimental study of Kolonin and Laptev (1982) (solubility and UV-Vis spectrophotometry) of Bi speciation under hydrothermal conditions:

- Bi^{3+} was selected as a basis species, with HKF parameters from Shock et al. (1997).
- HKF parameters for $Bi(OH)^{2+}$ and $Bi(OH)_4^-$ are from Shock et al. (1997).
- MRB parameters were regressed for $Bi(OH)_3$(aq), $Bi(OH)_2^+$, $BiCl_n^{3-n}$ (n=1-6), $Bi(OH)Cl_2$ (aq) and $Bi(OH)_2Cl$(aq) using association constants listed in Kolonin and Laptev (1982) (see Table DR4).

- Properties for $Bi_2S_2(OH)_2(aq)$, $HBi_2S_4^-$ and $H_2Bi_2S_4$ were generated by comparison with As and Sb complexes of similar stoichiometry (see Skirrow and Walshe, 2002).

The HKF properties for Au species ($AuHS_{(aq)}$, Au(HS)2$^-$, $Au(OH)_2^-$, $AuCl_2^-$) are from Bastrokov (2000), for $AuCl_{(aq)}$ and $Au(OH)_{(aq)}$ from Akinfiev and Zotov (2001). The thermodynamic properties for all other aqueous species are from the default HCh-UT database (Shvarov and Bastrakov 1999).

181 *Table DR4. Thermodynamic properties for Bi-OH and Bi-Cl complexes from Kolonin*
182 *and Laptev (1982).*

	25	75	200	300	Source*/note
Solubility data: 0.5 Bi_2O_3 + 1.5 H_2O = $Bi(OH)_3(aq)$	-6.06	-5.07	-3.50	-2.74	Tab. 1.
Log β3 = $\frac{[Bi(OH)_3^0]}{[Bi^{3+}][OH^-]^3}$	32.94 or 33.2	31.38	31.36	33.15	Tab. 1. The bridge to the 'basis' in HCh.
Log β2 = $\frac{[Bi(OH)_2^+]}{[Bi^{3+}][OH^-]^2}$	25.5	24.18	23.4	24.3	Tab. 1.
Log $\beta_1^{Cl} = \frac{[BiCl^{2+}]}{[Bi^{3+}][Cl^-]}$	2.2		3.7	5.7	Tab. 4.
Log $\beta_2^{Cl} = \frac{[BiCl_2^+]}{[Bi^{3+}][Cl^-]^2}$	3.5		4.9	7.2	Tab. 4.
Log $\beta_3^{Cl} = \frac{[BiCl_3^0]}{[Bi^{3+}][Cl^-]^3}$	5.8		6.9	9.3	Tab. 4.
Log $\beta_4^{Cl} = \frac{[BiCl_4^-]}{[Bi^{3+}][Cl^-]^4}$	6.75		7.8	10.5	Tab. 4.
Log $\beta_5^{Cl} = \frac{[BiCl_5^{2-}]}{[Bi^{3+}][Cl^-]^5}$	7.3		8.5	11.6	Tab. 4.
Log $\beta_6^{Cl} = \frac{[BiCl_6^{3-}]}{[Bi^{3+}][Cl^-]^6}$	7.36		9.0	12.4	Tab. 4.
Log $\beta_{1,2}^{OH,Cl} = \frac{[Bi(OH)Cl_2^0]}{[Bi^{3+}][OH][Cl^-]^2}$	16.0		16.0	18.2	Tab. 4.
Log $\beta_{2,1}^{OH,Cl} = \frac{[Bi(OH)_2Cl^0]}{[Bi^{3+}][OH]^2[Cl^-]}$	25.0		25.2	26.2	Tab. 4.

* Tables in Kolonin and Laptev (1981)

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