Electronic Supplementary Information

Why alloying with noble metals does not decrease the oxidation of platinum – a DFT-based ab-initio thermo-dynamics study

Alexander Kafka and Franziska Hess*

*Technische Universität Berlin,
Straße des 17. Juni 124, 10623 Berlin, Germany*

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Tab. S1: Structure, energy of formation (ΔE_f), emp. corrected standard enthalpy of formation ($\Delta H_f^0 - n_M \cdot 38.27 \; kJ/mol$) and standard entropy ($S^0$) of all crystalline and gaseous phases compared to selected literature values.

Phase	Structure	ΔE_f [kJ/mol]	ΔH_f^0 [kJ/mol]	$\Delta H_f^0 (Lit.)$ [kJ/mol]	S^0 [J/(mol·K)]	$S^0 (Lit.)$ [J/(mol·K)]
O_2	$D_{\infty h}$	0.00	0.00	---	205.43	205.15 [1]
H_2	$D_{\infty h}$	0.00	0.00	---	130.37	130.68 [1]
H_2O	C_{2v}	-121.72	-111.17	-121.92 [1]	94.47	94.42 [1]
Ag	$Fm\bar{3}m$	0.00	0.00	---	44.17	42.48 [2]
Ag_2O	$Pn\bar{3}m$	-5.91	-43.39	-15.34 [3]	62.51	60.95 [3]
Au	$Fm\bar{3}m$	0.00	0.00	---	51.20	47.35 [4], 47.29 [5]
Au_2O_3	$Fdd2$	-19.80	-55.16	---	56.86	---
α-Co	$P6_3/mmc$	0.00	0.00	---	27.47	30.04 [6], 30.03 [7]
β-Co	$Fm\bar{3}m$	1.44	1.33	---	29.43	30.66 [6]
CoO	$P2/m$ [a.)]	-126.51	-164.99	-236.86 [8], -237.39 [7]	48.68	54.31 [8], 53.33 [7]
Co_3O_4	$I4_1/amd$ [a.)]	-233.78	-268.87	-305.13 [8]	35.72	36.47 [8]
Pt_3Co	$Pm\bar{3}m$	-5.09	-5.12	---	51.06	---
PtCo	$P4/mmm$	-7.44	-7.50	---	71.24	---
Cu	$Fm\bar{3}m$	0.00	0.00	---	33.81	33.13 [9], 33.18[7]
Cu_2O	$Pn\bar{3}m$	-46.42	-83.45	-85.13 [10], -85.12 [7]	49.53	46.34 [10], 46.18 [7]
CuO	$C2/c$	-108.38	-145.32	-155.19 [10]	45.42	43.06 [10]
Pt_3Cu	$Cmmm$	-10.83	-10.83	---	52.46	---
PtCu	$R\bar{3}m$	-14.41	-14.41	---	75.09	---
Ir	$Fm\bar{3}m$	0.00	0.00	---	36.43	35.49 [11]
IrO_2	$P4_2/mnm$	-230.45	-263.05	-249.50 [12], -249.37 [13]	49.07	51.01 [13]
IrO_2	C_{2v}	192.16	190.66	188.20 [14]	286.07	274.11 [14]
IrO_3	C_{2v}	-9.88	-10.14	~ 22.00 [15 b.)]	330.23	303.20 [15 b.)]
Ni	$Fm\bar{3}m$	0.00	0.00	---	27.72	29.86 [16], 29.87 [7]
NiO	$P2/m$ [a.)]	-125.43	-163.34	-239.84 [17]	44.20	37.99 [7]
Pt_3Ni	$Pm\bar{3}m$	-5.90	-5.93	---	51.46	---
PtNi	$P4/mmm$	-8.68	-8.73	---	71.23	---
Pt	$Fm\bar{3}m$	0.00	0.00	---	42.07	41.53 [18]
PtO	$P4_2/mmc$	-42.80	-78.49	-88.50 [19]	45.87	---
Pt_3O_4	$Pm\bar{3}n$	-98.03	-133.09	-121.11 [19]	54.55	---
PtO_2	$P\bar{3}m1$	-134.26	-167.61	---	51.33	---
PtO_2	$Pnnm$	-147.67	-180.89	-191.00 [19]	50.43	---
PtO_2	C_{2v}	160.69	160.57	218.00 [20], ~164.00 [21-23]	259.89	~ 250.00 [21-23]
Re	$P6_3/mmc$	0.00	0.00	---	38.27	36.48 [24]
ReO_2	$P2_1/c$	-399.67	-433.09	---	50.52	---
ReO_2	$Pbcn$	-423.79	-456.67	-445.15 [25], -444.30 [26], -448.94 [27]	47.75	47.83 [25], 47.82 [27]
ReO_3	$Pm\bar{3}m$	-608.26	-640.03	-601.90 [28], -589.11 [27]	67.97	69.25 [27]
Re_2O_7	$P2_12_12_1$	-637.68	-667.39	-631.58 [27]	104.20	103.64 [27]
Re_2O_7	C_{2v}	-572.58	-567.95	-566.30 [28]	235.01	219.35 [28]
Rh	$Fm\bar{3}m$	0.00	0.00	---	32.01	31.56 [11]
Rh_2O_3	$Pbca$	-173.12	-207.77	-202.77 [29], -202.98 [30]	39.63	37.85 [29], 35.75 [30]
Rh_2O_3	$R\bar{3}c$	-170.66	-205.34	---	39.67	---
RhO_2	$P4_2/mnm$	-243.29	-276.41	-244.94 [31]	46.05	45.11 [31]
RhO_2	C_{2v}	174.61	173.23	188.87 [21,22], 200.13 [23]	255.32	257.30 [21,22], 264.40 [23]

a.) The $Fd\bar{3}m$- and $Fm\bar{3}m$-structures of Co_3O_4 and CoO / NiO are distorted due to their magnetic structure.

b.) and references therein

Tab. S1: Structure, energy of formation (ΔE_f), emp. corrected standard enthalpy of formation ($\Delta H_f^0 - n_M \cdot 38.27 \ kJ/mol$) and standard entropy ($S^0$) of all crystalline and gaseous phases compared to selected literature values.(continued)

Phase	Structure	ΔE_f [kJ/mol]	ΔH_f^0 [kJ/mol]	$\Delta H_f^0(Lit.)$ [kJ/mol]	S^0 [J/(mol·K)]	$S^0(Lit.)$ [J/(mol·K)]
W	$Im\bar{3}m$	0.00	0.00	---	34.04	32.66 [32]
WO$_2$	$P2_1/c$	-562.31	-596.16	-586.55 [33], -589.69 [1]	50.84	50.53 [1]
WO$_2$	C_{2v}	25.24	24.78	~76.57 [1]	273.53	285.50 [1]
W$_{18}$O$_{49}$	$P2/m$	-759.66	-792.31	-779.70 [33], -781.15 [1]	67.21	68.43 [1]
WO$_3$	$P2_1/c$	-822.09	-853.90	---	78.45	---
WO$_3$	$Pnma$	-821.66	-853.34	-842.91 [1,33]	80.15	76.57 [34], 75.91 [1]
WO$_3$	$P4/ncc$	-820.59	-853.29	---	78.98	---
WO$_3$	C_{3v}	-326.08	-325.04	~ -292.88 [1]	290.70	286.44 [1]
Pt$_2$W	$Immm$	-34.46	-34.47	---	56.85	---
PtW	$P\bar{6}m2$	-10.70	-10.73	---	77.26	---

a.) The $Fd\bar{3}m$- and $Fm\bar{3}m$-structures of Co$_3$O$_4$ and CoO / NiO are distorted due to their magnetic structure.

b.) and references therein

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Tab. S2: Fit parameters obtained for the vibrational heat capacity $C_{vib}(T)$, enthalpy $H_{vib}(T)$ and entropy $S_{vib}(T)$ of all crystalline phases between 300 K and 1300 K per formula unit. The corrected single-point energy E_{corr} already contains the mean empirical correction of 38.27 kJ/mol per metal atom. Please see below, how the parameters are related.

Phase	Structure	E_{corr} [kJ/mol]	a_1 [J/(mol·K)]	a_2 [J/(mol·K²)]	a_3 [J/(mol·K³)]	a_4 [J/(mol·K⁴)]	a_5 [J·K/mol]	a_6 [J/mol]	a_7 [J/(mol·K)]
Ag	$Fm\bar{3}m$	-318.27	2.336E+01	4.863E-03	-5.140E-06	1.799E-09	9.966E-01	4.616E+02	-9.016E+01
Ag$_2$O	$Pn\bar{3}m$	-1200.57	5.028E+01	7.168E-02	-7.345E-05	2.519E-08	9.597E-01	7.883E+03	-1.798E+02
Au	$Fm\bar{3}m$	-373.10	2.396E+01	3.038E-03	-3.214E-06	1.125E-09	9.978E-01	2.875E+02	-8.606E+01
Au$_2$O$_3$	$Fdd2$	-2289.35	5.226E+01	2.088E-01	-2.123E-04	7.246E-08	9.989E-01	2.381E+04	-2.375E+02
α-Co	$P6_3/mmc$	-719.52	1.921E+01	1.747E-02	-1.836E-05	6.400E-09	9.881E-01	1.705E+03	-8.640E+01
β-Co	$Fm\bar{3}m$	-718.08	2.015E+01	1.463E-02	-1.540E-05	5.375E-09	9.899E-01	1.417E+03	-8.910E+01
CoO	$P2/m$	-1359.96	3.049E+01	5.367E-02	-5.584E-05	1.935E-08	9.661E-01	5.498E+03	-1.388E+02
Co$_3$O$_4$	$I4_1/amd$	-4877.38	5.069E+01	3.589E-01	-3.660E-04	1.252E-07	9.981E-01	4.035E+04	-2.735E+02
Pt$_3$Co	$Pm\bar{3}m$	-2726.33	8.933E+01	3.201E-02	-3.378E-05	1.181E-08	9.776E-01	3.061E+03	-3.640E+02
PtCo	$P4/mmm$	-1396.55	4.328E+01	2.022E-02	-2.131E-05	7.444E-09	9.860E-01	1.945E+03	-1.805E+02
Cu	$Fm\bar{3}m$	-416.84	2.134E+01	1.101E-02	-1.161E-05	4.054E-09	9.924E-01	1.060E+03	-9.060E+01
Cu$_2$O	$Pn\bar{3}m$	-1478.72	4.254E+01	9.222E-02	-9.324E-05	3.170E-08	9.995E-01	1.077E+04	-1.670E+02
CuO	$C2/c$	-1039.15	2.610E+01	6.996E-02	-7.208E-05	2.481E-08	9.590E-01	7.513E+03	-1.212E+02
Pt$_3$Cu	$Cmmm$	-2446.61	9.015E+01	2.952E-02	-3.116E-05	1.089E-08	9.793E-01	2.819E+03	-3.638E+02
PtCu	$R\bar{3}m$	-1107.82	4.419E+01	1.744E-02	-1.840E-05	6.429E-09	9.879E-01	1.674E+03	-1.811E+02
Ir	$Fm\bar{3}m$	-923.97	2.228E+01	8.177E-03	-8.632E-06	3.019E-09	9.943E-01	7.805E+02	-9.258E+01
IrO$_2$	$P4_2/mnm$	-2144.03	1.837E+01	1.580E-01	-1.577E-04	5.315E-08	9.993E-01	1.953E+04	-9.614E+01
Ni	$Fm\bar{3}m$	-573.18	1.926E+01	1.729E-02	-1.817E-05	6.336E-09	9.883E-01	1.688E+03	-8.644E+01
NiO	$P2/m$	-1212.55	3.057E+01	5.796E-02	-6.040E-05	2.094E-08	9.631E-01	5.897E+03	-1.448E+02
Pt$_3$Ni	$Pm\bar{3}m$	-2583.23	8.933E+01	3.201E-02	-3.378E-05	1.181E-08	9.776E-01	3.063E+03	-3.627E+02
PtNi	$P4/mmm$	-1252.68	4.312E+01	2.068E-02	-2.180E-05	7.614E-09	9.857E-01	1.992E+03	-1.797E+02
Pt	$Fm\bar{3}m$	-662.15	2.296E+01	6.085E-03	-6.426E-06	2.248E-09	9.957E-01	5.796E+02	-9.030E+01
PtO	$P4_2/mmc$	-1218.89	2.044E+01	8.445E-02	-8.560E-05	2.915E-08	9.996E-01	9.754E+03	-9.224E+01
Pt$_3$O$_4$	$Pm\bar{3}n$	-4298.03	6.990E+01	2.884E-01	-2.872E-04	9.666E-08	9.987E-01	3.594E+04	-3.087E+02
PtO$_2$	$P\bar{3}m1$	-1786.02	1.877E+01	1.611E-01	-1.635E-04	5.574E-08	9.992E-01	1.850E+04	-9.687E+01
PtO$_2$	$Pnnm$	-1799.44	2.036E+01	1.546E-01	-1.556E-04	5.278E-08	9.992E-01	1.839E+04	-1.052E+02
Re	$P6_3/mmc$	-1261.66	2.238E+01	7.382E-03	-7.794E-06	2.725E-09	9.948E-01	7.046E+02	-9.114E+01
ReO$_2$	$P2_1/c$	-2650.94	2.253E+01	1.479E-01	-1.487E-04	5.038E-08	9.993E-01	1.777E+04	-1.158E+02
ReO$_2$	$Pbcn$	-2675.06	1.948E+01	1.560E-01	-1.564E-04	5.289E-08	9.992E-01	1.892E+04	-1.033E+02
ReO$_3$	$Pm\bar{3}m$	-3335.20	2.926E+01	1.963E-01	-1.959E-04	6.608E-08	9.991E-01	2.433E+04	-1.491E+02
Re$_2$O$_7$	$P2_12_12_1$	-7204.91	7.786E+01	3.644E-01	-3.438E-04	1.117E-07	9.989E-01	5.656E+04	-3.295E+02
Rh	$Fm\bar{3}m$	-764.58	2.110E+01	1.175E-02	-1.239E-05	4.327E-09	9.918E-01	1.130E+03	-9.122E+01
Rh$_2$O$_3$	$Pbca$	-3378.95	3.661E+01	2.544E-01	-2.590E-04	8.847E-08	9.986E-01	2.884E+04	-1.944E+02
Rh$_2$O$_3$	$R\bar{3}c$	-3374.05	3.671E+01	2.544E-01	-2.591E-04	8.851E-08	9.986E-01	2.877E+04	-1.949E+02
RhO$_2$	$P4_2/mnm$	-1997.48	1.898E+01	1.580E-01	-1.588E-04	5.378E-08	9.992E-01	1.896E+04	-1.026E+02
W	$Im\bar{3}m$	-1323.22	2.162E+01	1.017E-02	-1.073E-05	3.748E-09	9.929E-01	9.754E+02	-9.174E+01
WO$_2$	$P2_1/c$	-2875.14	2.370E+01	1.453E-01	-1.465E-04	4.972E-08	9.993E-01	1.724E+04	-1.214E+02
W$_{18}$O$_{49}$	$P2/m$	-61488.57	5.522E+02	3.128E+00	-3.123E-03	1.053E-06	9.852E-01	3.885E+05	-2.740E+03
WO$_3$	$P2_1/c$	-3610.59	3.594E+01	1.713E-01	-1.674E-04	5.570E-08	9.993E-01	2.332E+04	-1.705E+02
WO$_3$	$Pnma$	-3610.16	3.668E+01	1.699E-01	-1.658E-04	5.511E-08	9.993E-01	2.329E+04	-1.726E+02
WO$_3$	$P4/ncc$	-3610.59	3.594E+01	1.713E-01	-1.674E-04	5.570E-08	9.993E-01	2.332E+04	-1.705E+02
Pt$_2$W	$Immm$	-2750.89	6.727E+01	2.274E-02	-2.401E-05	8.397E-09	9.840E-01	2.170E+03	-2.753E+02
PtW	$P\bar{6}m2$	-2006.78	4.503E+01	1.491E-02	-1.574E-05	5.503E-09	9.895E-01	1.423E+03	-1.831E+02

$$G(T) = H(T) + TS(T) = E_{corr} + H_{vib}(T) - TS_{vib}(T)$$

$$C_{vib}(T) = a + bT + cT^2 + dT^3 - e/T^2$$

$$H_{vib}(T) = aT + bT^2/2 + cT^3/3 + dT^4/4 - e/T + f$$

$$S_{vib}(T) = a\ln(T) + bT + cT^2/2 + dT^3/3 - e/2T^2 + g$$

Tab. S3: Comparison of several dispersion correction methods available in VASP 5 and VASP 6 for the Pt(II)-oxides. All calculations employed the PBE functional. While the energies of formation (ΔE_f) listed here are not directly comparable to experimental data, none of the methods except PBE-D3/BJ provides a reasonable estimate for the enthalpy of formation of gaseous PtO$_2$ (see Tab. S1), which is critical for this investigation. At the same time, based on the c-lattice parameter PBE-D3/BJ determines the best geometries.

	O$_2$	Pt	α-PtO$_2$			β-PtO$_2$			PtO$_2$(g)		
	E	E	c	E	ΔE_f	c	E	ΔE_f	c	E	ΔE_f
	[kJ/mol]	[kJ/mol]	[Å]	[kJ/mol]	[kJ/mol]	[Å]	[kJ/mol]	[kJ/mol]	[Å]	[kJ/mol]	[kJ/mol]
EXP	---	---	3.92 [1]	---	---	4.16 [2]	---	---	3.14 [3]	---	---
PBE	-951.34	-587.75	3.97	-1684.36	-145.28	4.63	-1685.72	-146.63	3.18	-1449.60	89.49
MBD@rSC/FI	-951.34	-587.73	3.97	-1684.88	-145.81	4.78	-1685.93	-146.86	3.18	-1449.60	89.47
DDsC	-951.34	-587.73	3.97	-1684.88	-145.81	4.78	-1685.93	-146.86	3.18	-1449.60	89.47
TS/HI	-951.34	-635.78	3.93	-1727.13	-140.01	4.23	-1739.30	-152.17	3.17	-1449.97	137.16
D3/BJ	-952.04	-661.45	3.92	-1747.75	-134.26	4.15	-1761.17	-147.67	3.17	-1453.51	159.99
BEEF-vdW	-603.08	-296.15	3.99	-1056.97	-157.74	4.39	-1062.35	-163.13	3.19	-780.99	118.24
vdW-DF2	-582.73	-251.95	4.11	-1039.39	-204.71	4.22	-1054.37	-219.69	3.26	-819.78	14.90
optB86b-vdW	-605.81	-368.68	3.95	-1156.50	-182.01	4.07	-1170.74	-196.25	3.17	-842.11	132.37

1   R. W. G. Wyckoff, *Crystal Structures*, Interscience Publishers, New York, 2nd edn., 1963, **1**, 7–83.

2   H. R. Hoekstra, S. Siegel and F. X. Gallagher, *Advances in Chemistry*, American Chemical Society, Washington, D.C., 1971, **98**, 39–53.

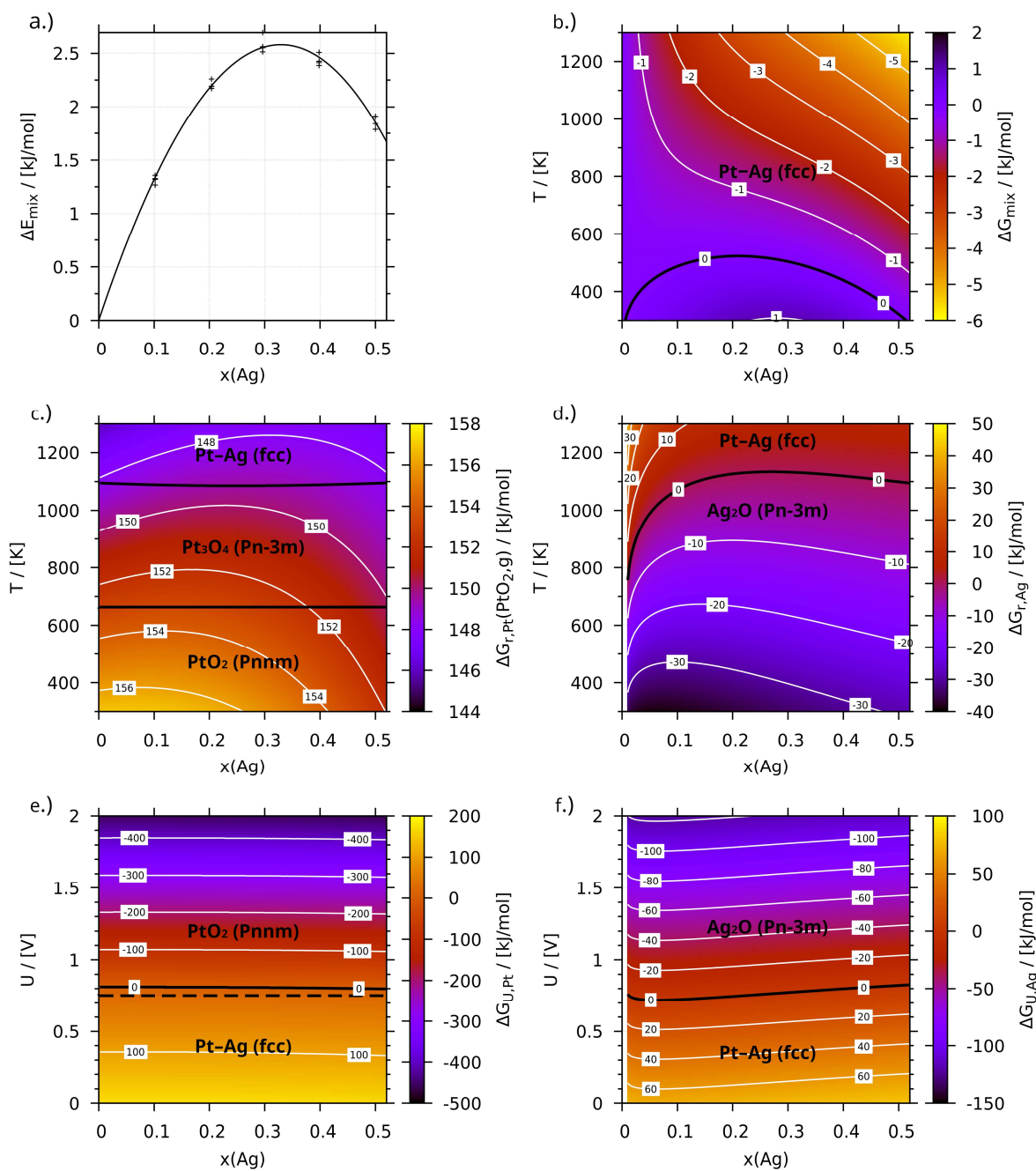3   K.-J. Range, F. Rau, U. Klement, A. M. Heyns, *Mater. Res. Bull.*, 1987, **22**, 1541–1547.

Fig. S1: Mixing energy (a), Gibbs free energy of mixing (b), Gibbs free energy of PtO_2 formation (c), Gibbs free energy of silver oxidation (d), Gibbs free energy of electrochemical platinum oxidation (pH=0, T=298.15 K) (e) and Gibbs free energy of electrochemical silver oxidation (pH=0, T=298.15 K) (f) of Pt–Ag. Phases and their boundaries are signified in black.
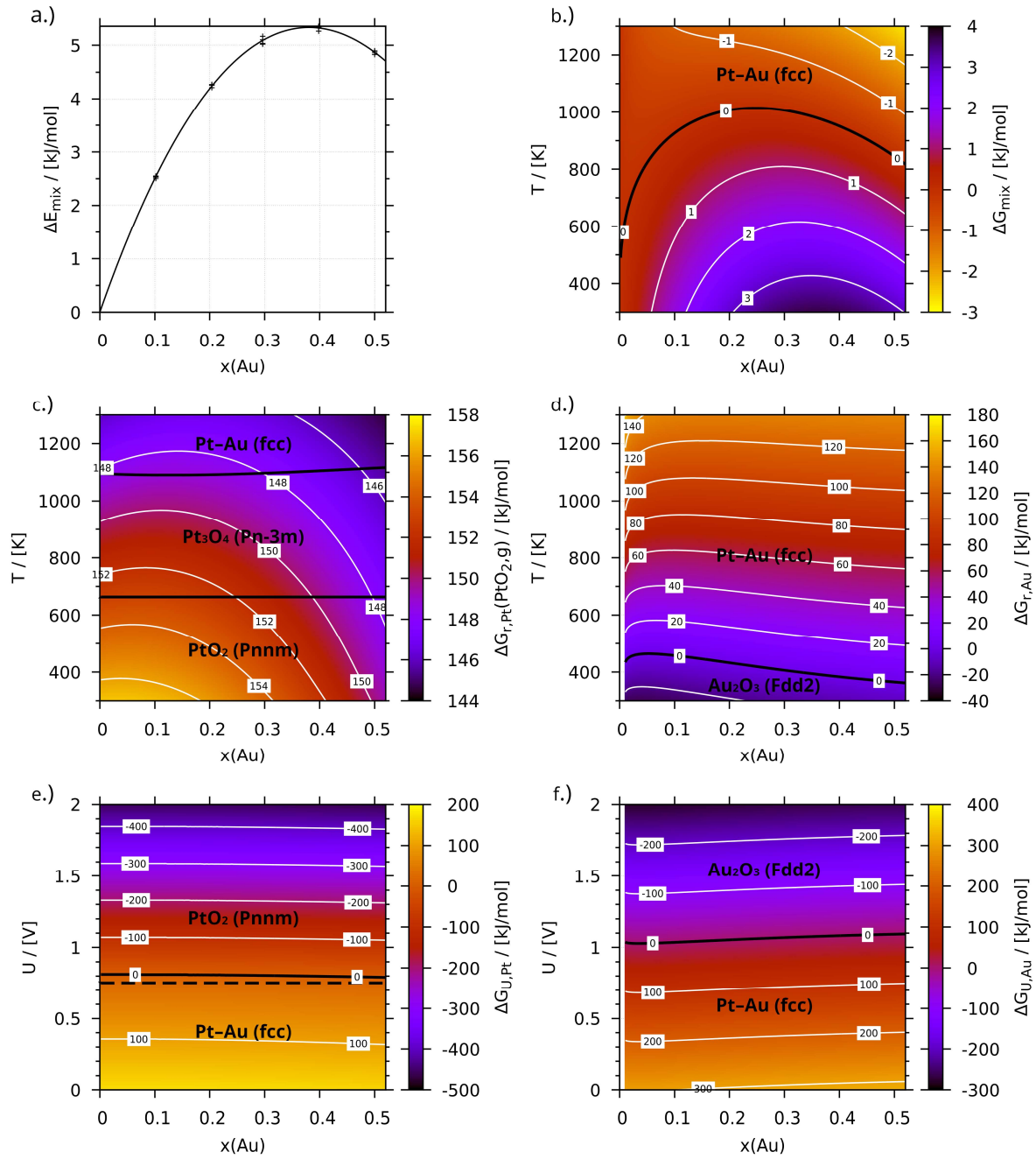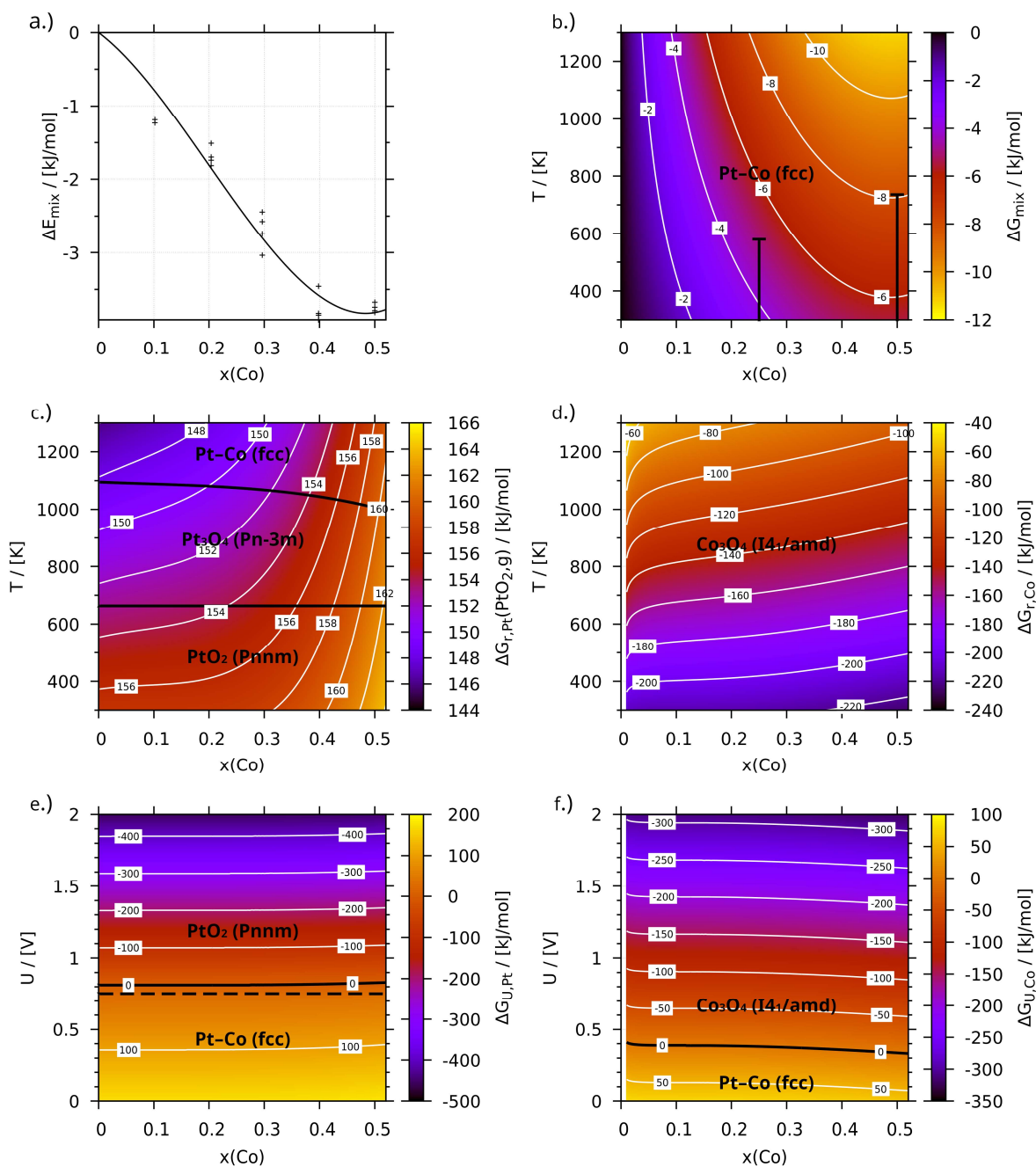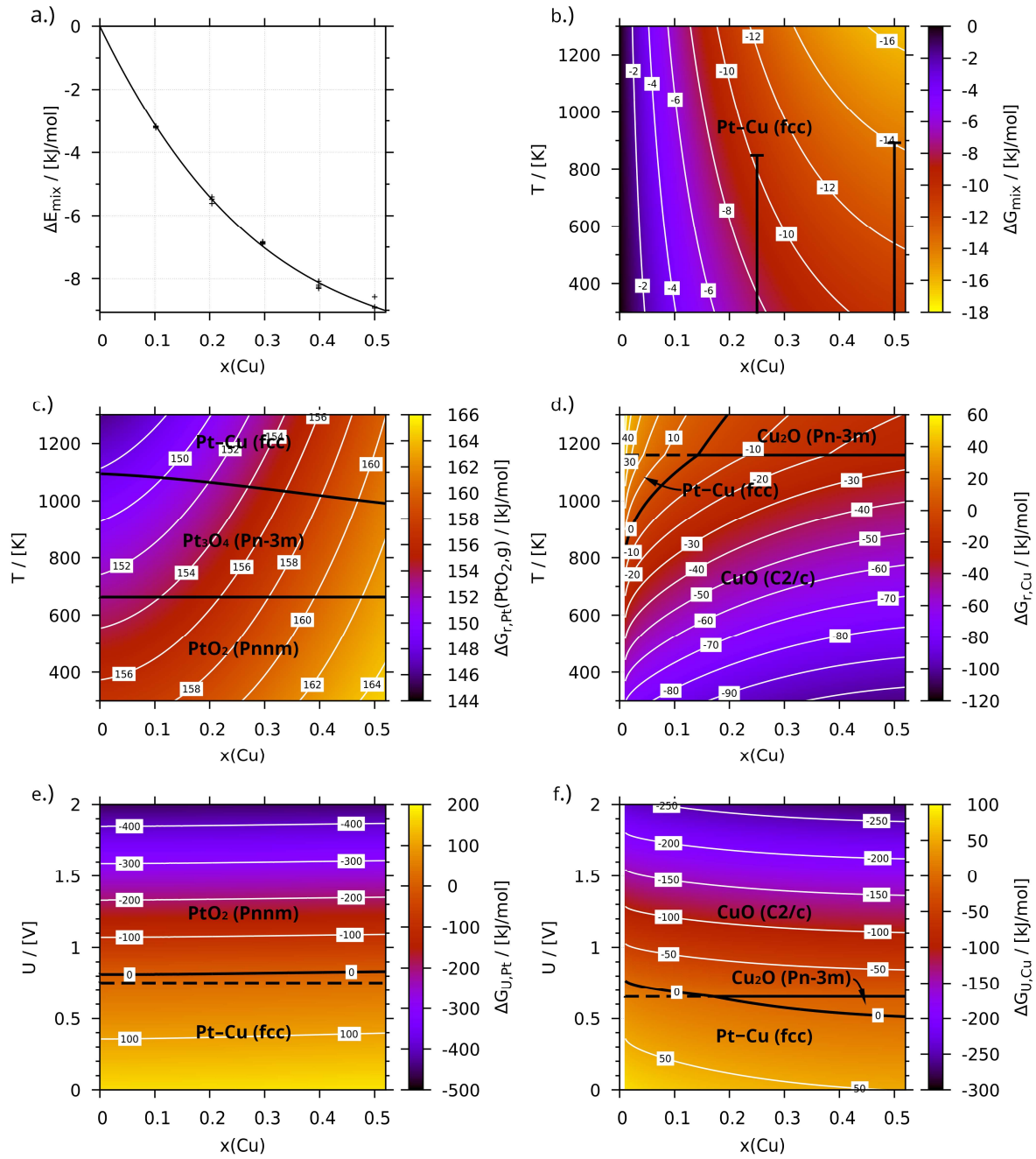
Fig. S2: Mixing energy (a), Gibbs free energy of mixing (b), Gibbs free energy of PtO₂ formation (c), Gibbs free energy of gold oxidation (d), Gibbs free energy of electrochemical platinum oxidation (*pH*=0, *T*=298.15 K) (e) and Gibbs free energy of electrochemical gold oxidation (*pH*=0, *T*=298.15 K) (f) of Pt–Au. Phases and their boundaries are signified in black.

Fig. S3: Mixing energy (a), Gibbs free energy of mixing (b), Gibbs free energy of PtO$_2$ formation (c), Gibbs free energy of cobalt oxidation (d), Gibbs free energy of electrochemical platinum oxidation (pH=0, T=298.15 K) (e) and Gibbs free energy of electrochemical cobalt oxidation (pH=0, T=298.15 K) (f) of Pt–Co. Phases and their bou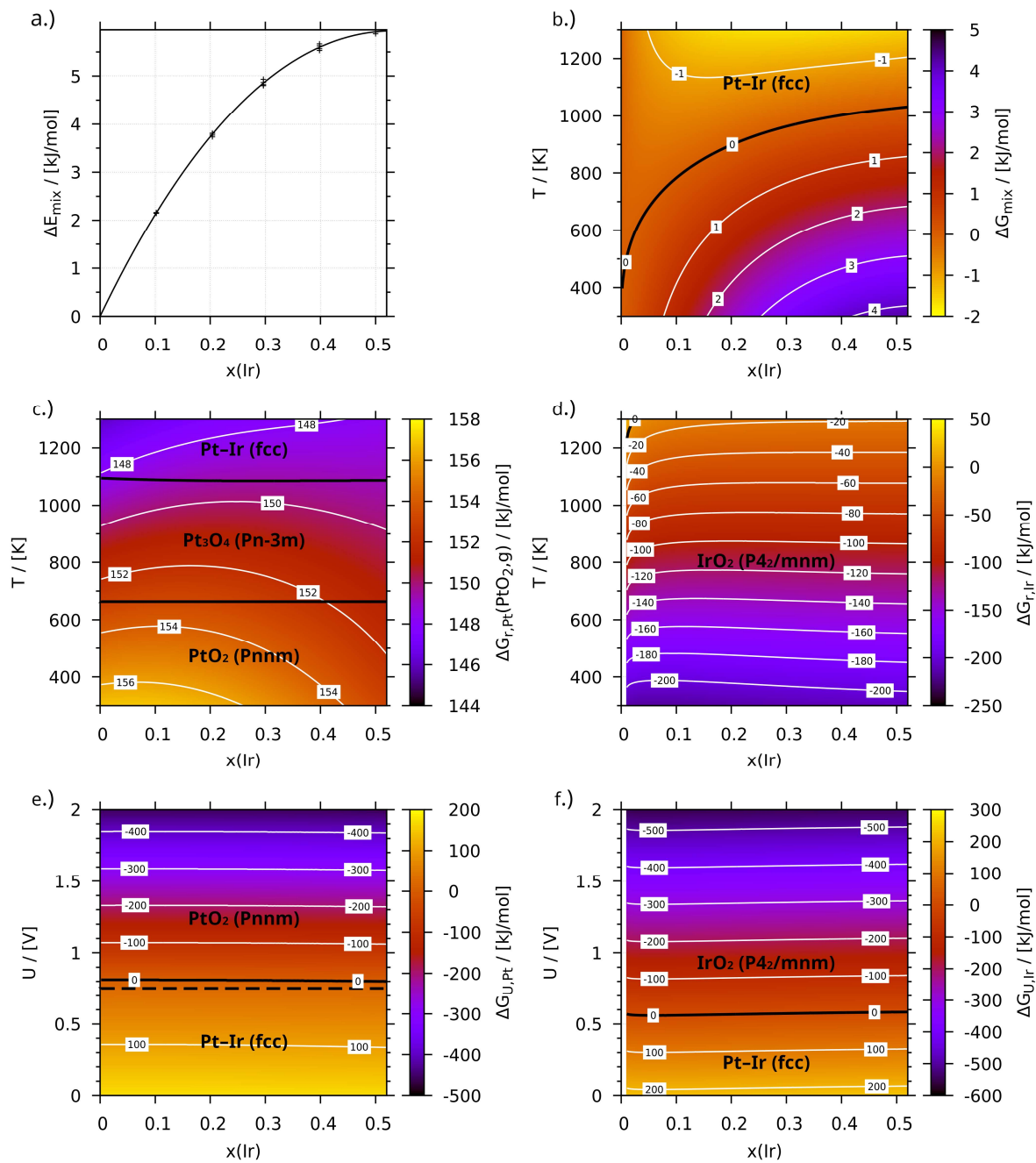ndaries are signified in black. The $Fd\overline{3}m$-structure of Co$_3$O$_4$ is deformed due to its magnetic structure.

Fig. S4: Mixing energy (a), Gibbs free energy of mixing (b), Gibbs free energy of PtO$_2$ formation (c), Gibbs free energy of copper oxidation (d), Gibbs free energy of electrochemical platinum oxidation (pH=0, T=298.15 K) (e) and Gibbs free energy of electrochemical copper oxidation (pH=0, T=298.15 K) (f) of Pt–Cu. Phases and their boundaries are signified in black.

Fig. S5: Mixing energy (a), Gibbs free energy of mixing (b), Gibbs free energy of PtO₂ formation (c), Gibbs free energy of iridium oxidation (d), Gibbs free energy of electrochemical platinum oxidation (*pH*=0, *T*=298.15 K) (e) and Gibbs free energy of electrochemical iridium oxidation (*pH*=0, *T*=298.15 K) (f) of Pt–Ir. Phases and their boundaries are signified in black.
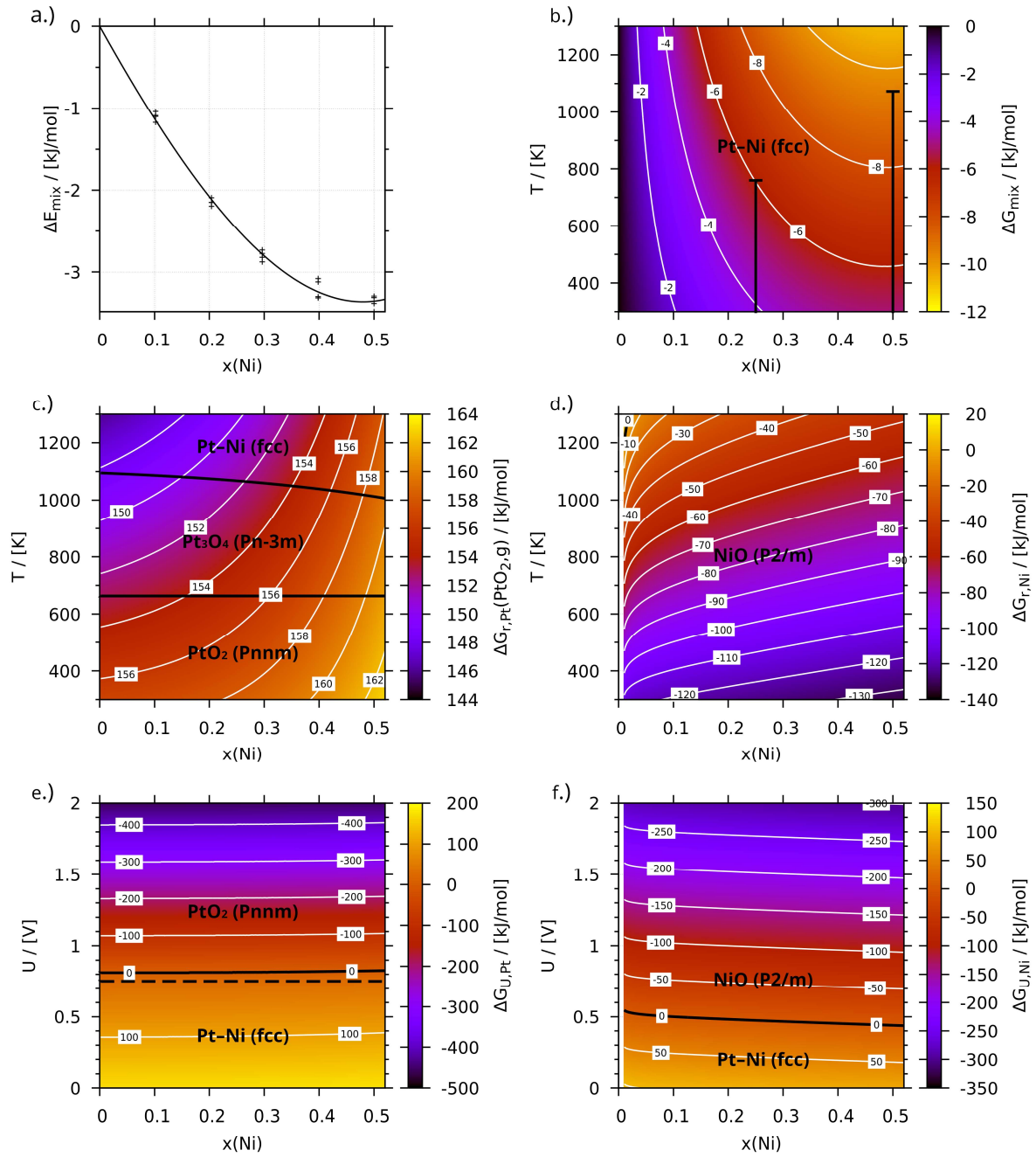
Fig. S6: Mixing energy (a), Gibbs free energy of mixing (b), Gibbs free energy of PtO₂ formation (c), Gibbs free energy of nickel oxidation (d), Gibbs free energy of electrochemical platinum oxidation (*pH*=0, *T*=298.15 K) (e) and Gibbs free energy of electrochemical nickel oxidation (*pH*=0, *T*=298.15 K) (f) of Pt–Ni. Phases and their boundaries are signified in black. The $Fm\bar{3}m$-structure of NiO is distorted due to its magnetic structure.
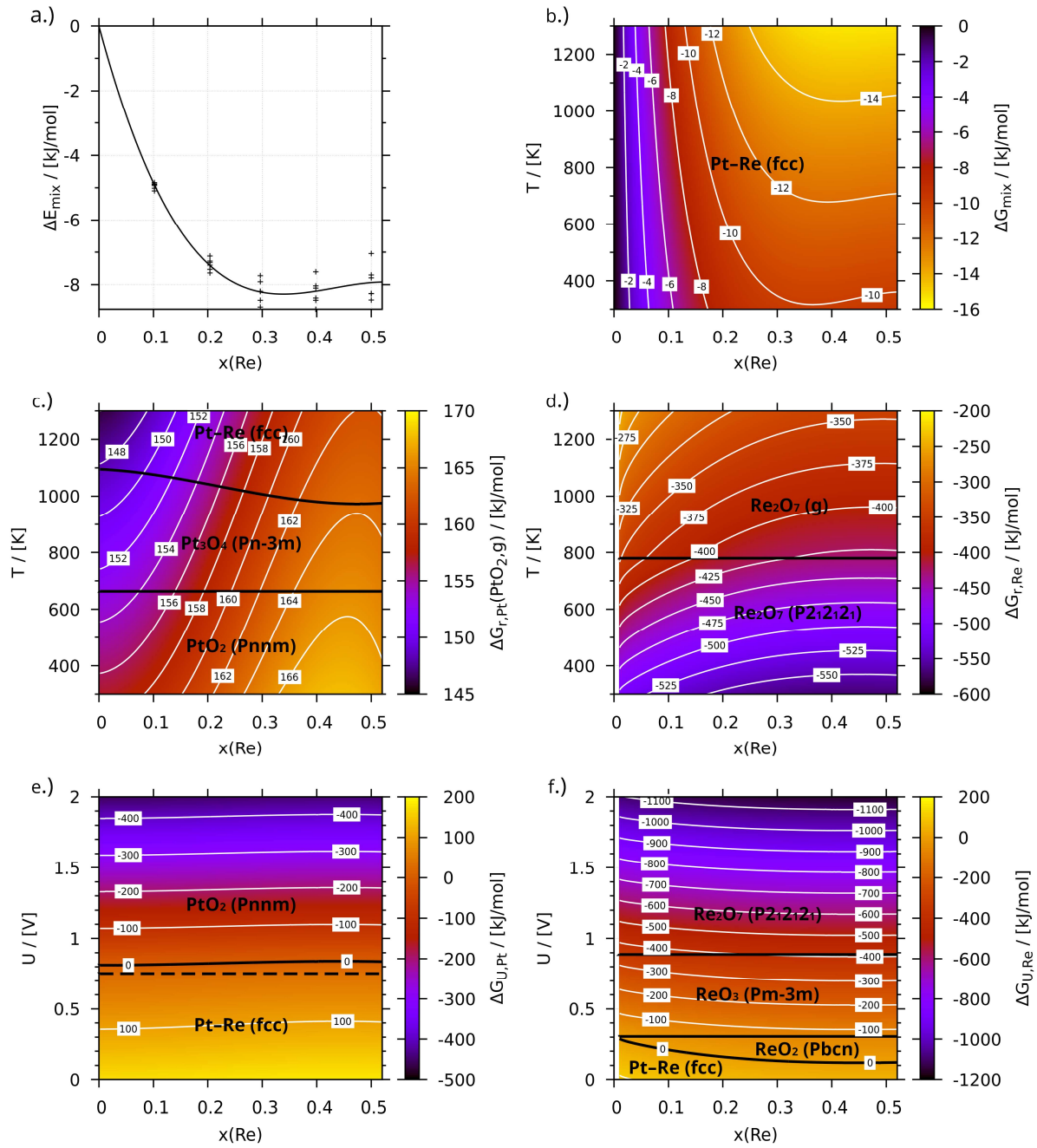
Fig. S7: Mixing energy (a), Gibbs free energy of mixing (b), Gibbs free energy of PtO$_2$ formation (c), Gibbs free energy of rhenium oxidation (d), Gibbs free energy of electrochemical platinum oxidation (*pH*=0, *T*=298.15 K) (e) and Gibbs free energy of electrochemical rhenium oxidation (*pH*=0, *T*=298.15 K) (f) of Pt–Re. Phases and their boundaries are signified in black.
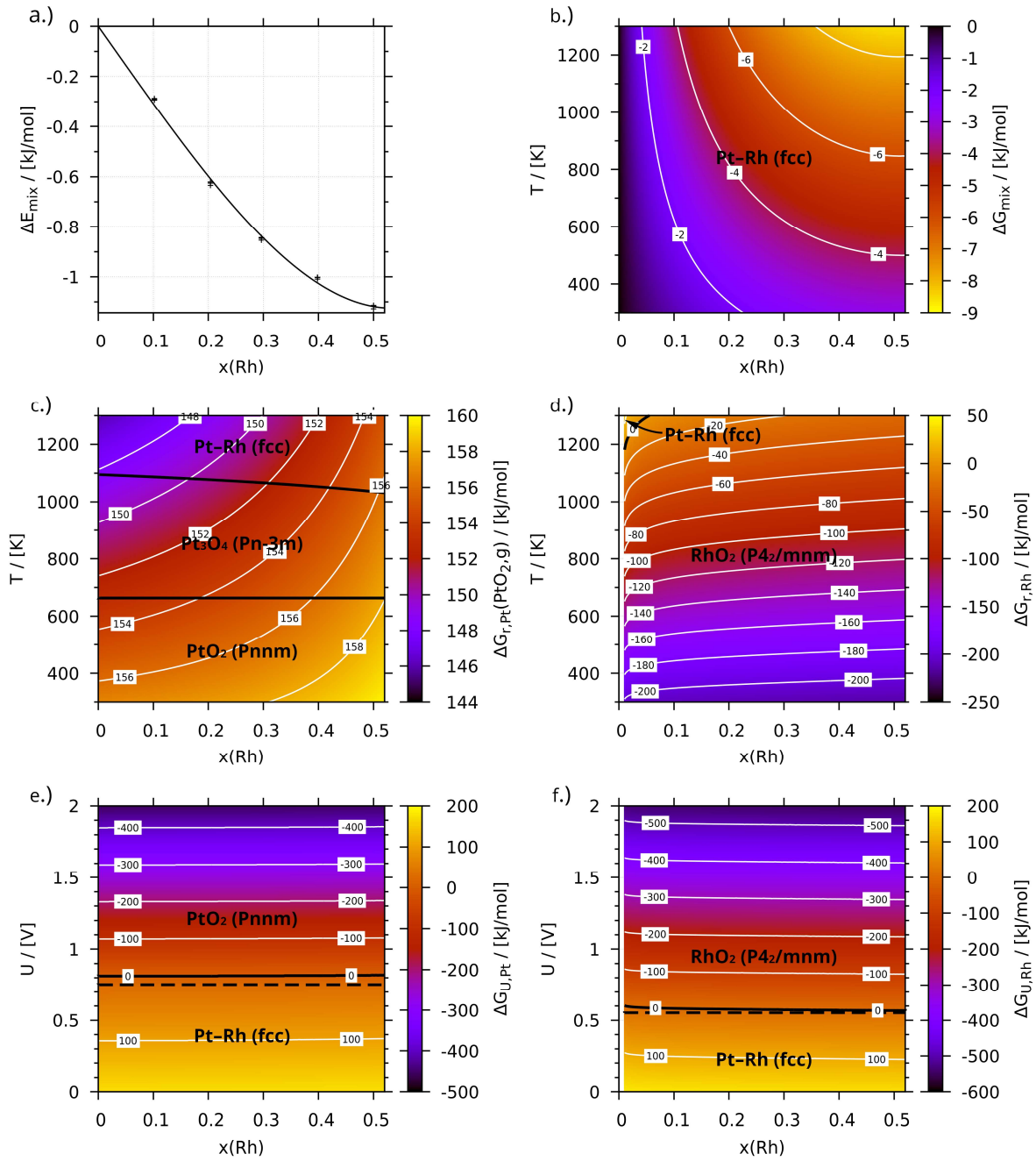
Fig. S8: Mixing energy (a), Gibbs free energy of mixing (b), Gibbs free energy of PtO_2 formation (c), Gibbs free energy of rhodium oxidation (d), Gibbs free energy of electrochemical platinum oxidation (pH=0, T=298.15 K) (e) and Gibbs free energy of electrochemical rhodium oxidation (pH=0, T=298.15 K) (f) of Pt–Rh. Phases and their boundaries are signified in black.
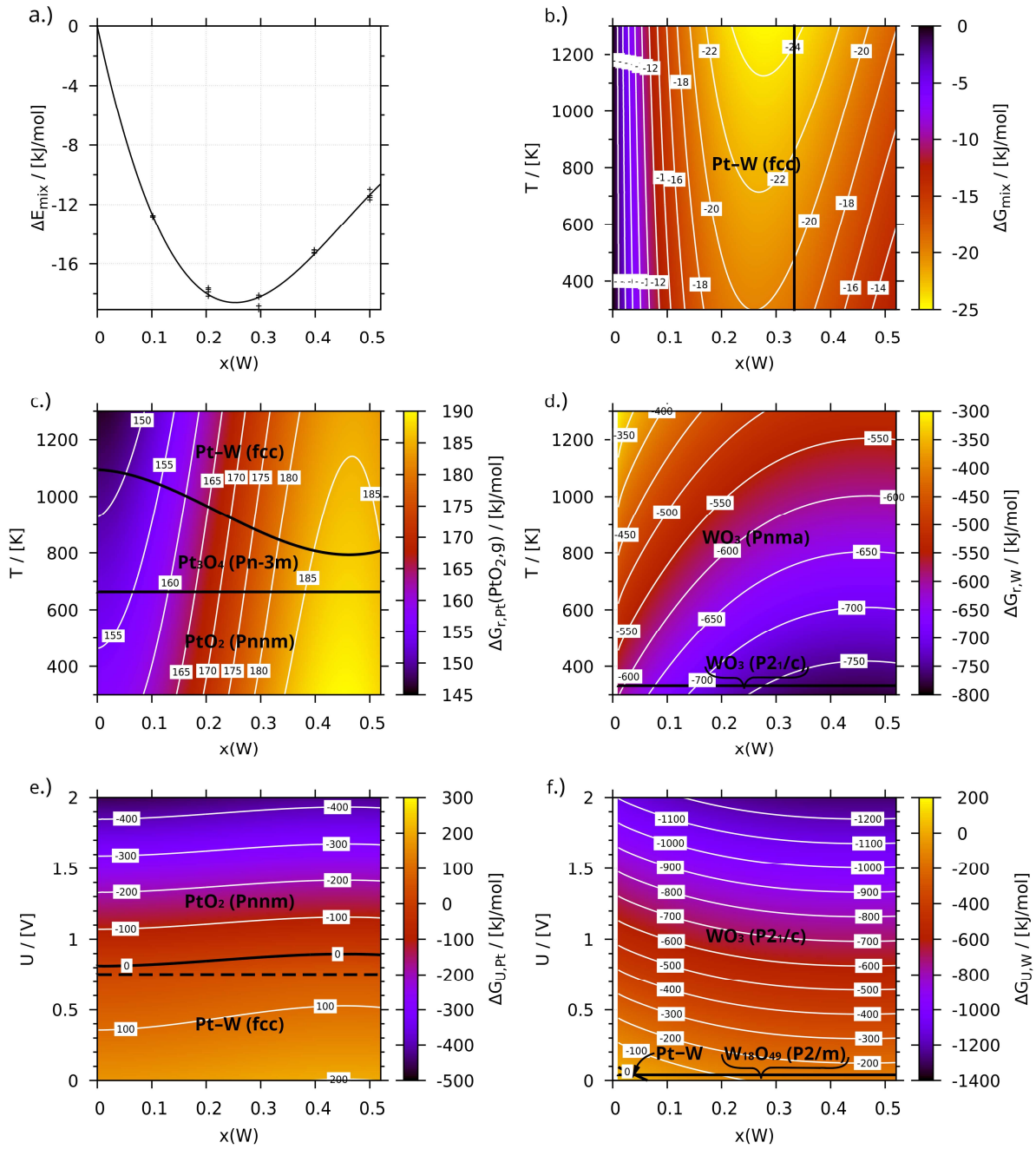
Fig. S9: Mixing energy (a), Gibbs free energy of mixing (b), Gibbs free energy of PtO₂ formation (c), Gibbs free energy of tungsten oxidation (d), Gibbs free energy of electrochemical platinum oxidation (*pH*=0, *T*=298.15 K) (e) and Gibbs free energy of electrochemical tungsten oxidation (*pH*=0, *T*=298.15 K) (f) of Pt–W. Phases and their boundaries are signified in black.
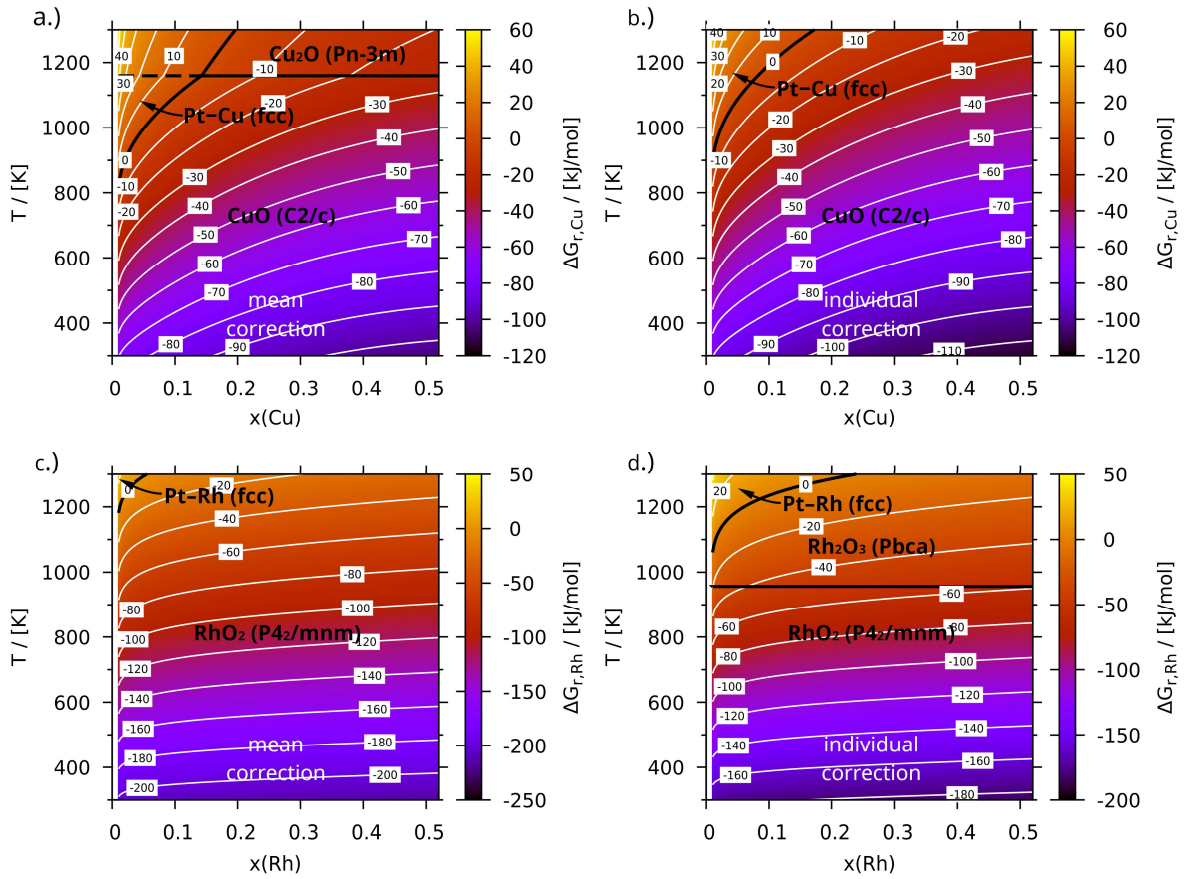
Fig. S10: Gibbs free energy of copper- (a,b) and rhodium oxidation (c,d) with mean empirical and individual correction based on the oxide enthalpies of formation. Phases and their boundaries are signified in black.