Supporting information

Highly selective capture of palladium from acidic solution by sulfur-functionalized porous carbon microsphere: Performance and mechanism

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Text S1. Reagent

Sucrose (AR, 99.5%), potassium hydroxide (AR, ≥85.0%), ammonium sulfate (AR, 99.0%), and nitric acid (AR, 65-68%) were purchased from Xilong Science Co., Ltd, Palladium nitrate dihydrate (AR) was purchased from Shanghai McLean Biochemical Technology Co., Ltd, The standard solutions (1000 mg/L) of In, Sc, Ge, Rh, Bi, Y, Li, Na, Al, Ca, Cr, Mn, Fe, Co, Ni, Cu, Zn, Zr, Mo, Pd, Cd, Te, Ba, La, Ce, Nd, Pb, Ru, K, Mg, Ti, and Nb were all purchased from Tanmo Quality Inspection Technology Co., Ltd, Nitrate compounds (Na, Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, Cd, La, Ce, Pb, K, Mg) simulating the competing ions in the acidic wastewater of spent fuel were purchased from Xilong Science Co., Ltd.

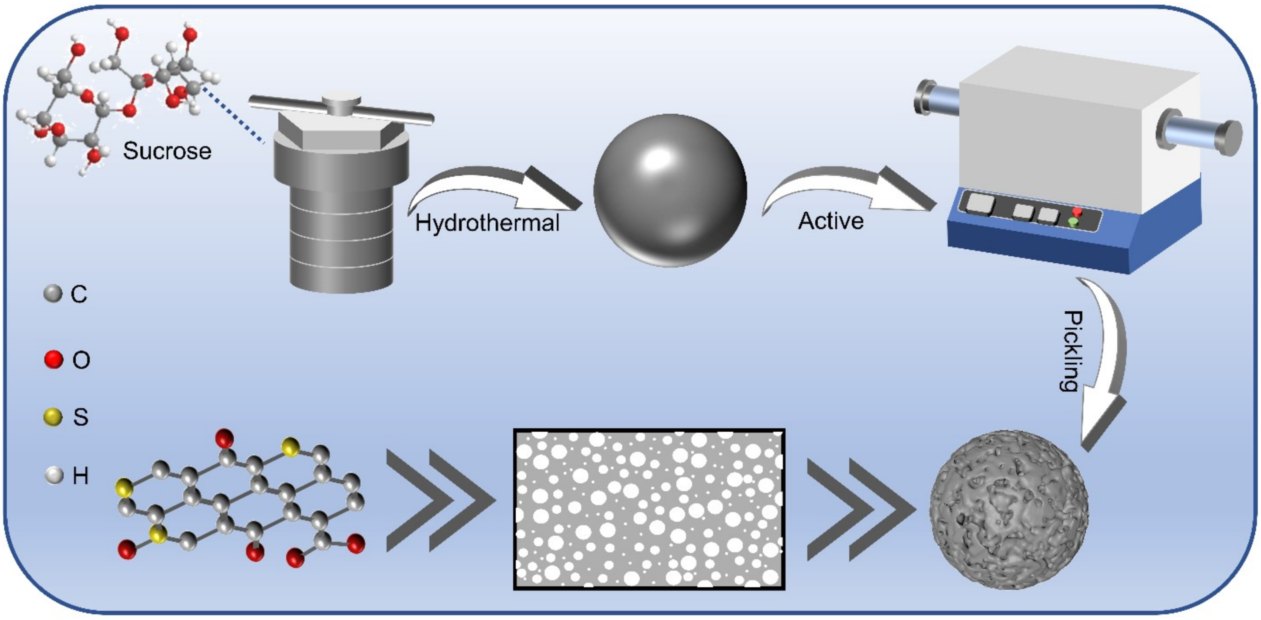

Fig. S1. The synthesis process of the SPCM.

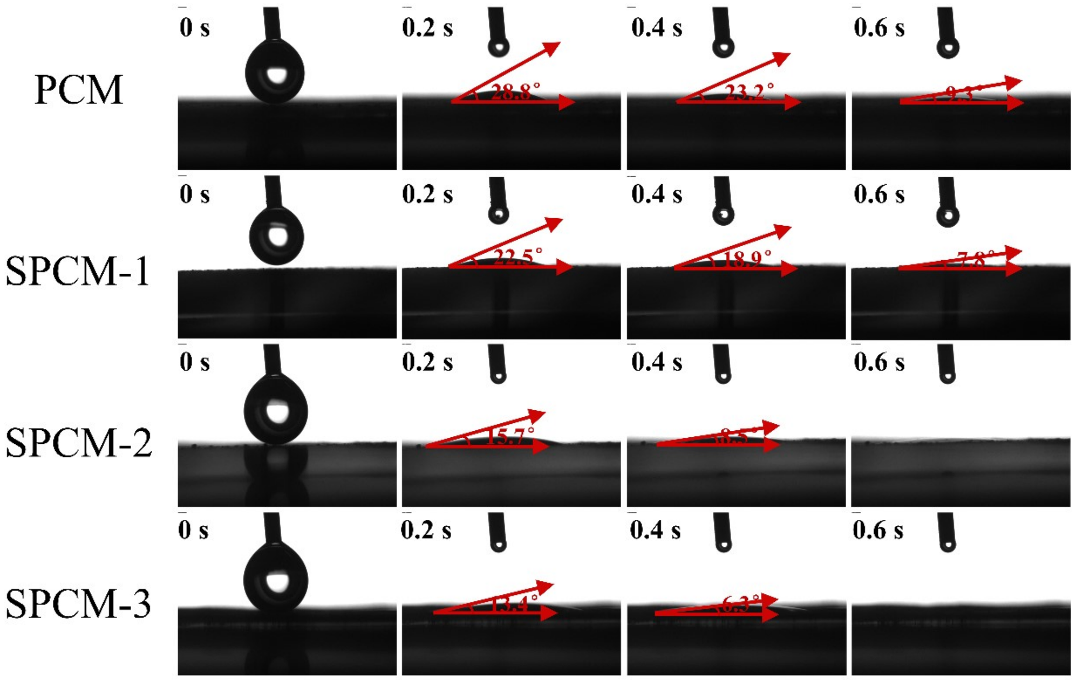

Fig. S2. Contact angles of the as-prepared carbon samples.

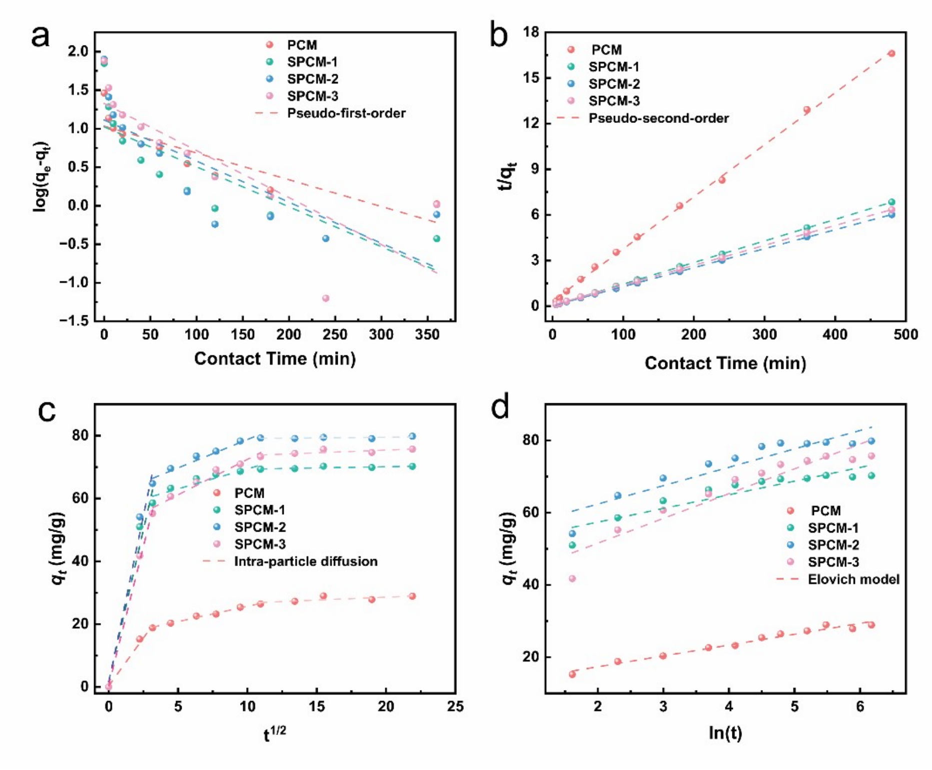

Fig. S3. Adsorption kinetics of Pd(II) on as-prepared carbon samples. a) Pseudo-first-order kinetic model, b) Pseudo-second-order kinetic model, c) Intra-particle diffusion kinetic model, d) Elovich kinetic model. ([sorbent] = 200 mg/L, Pd(II) = 40 mg/L, [HNO_3] = 1 M, T = 35 °C).

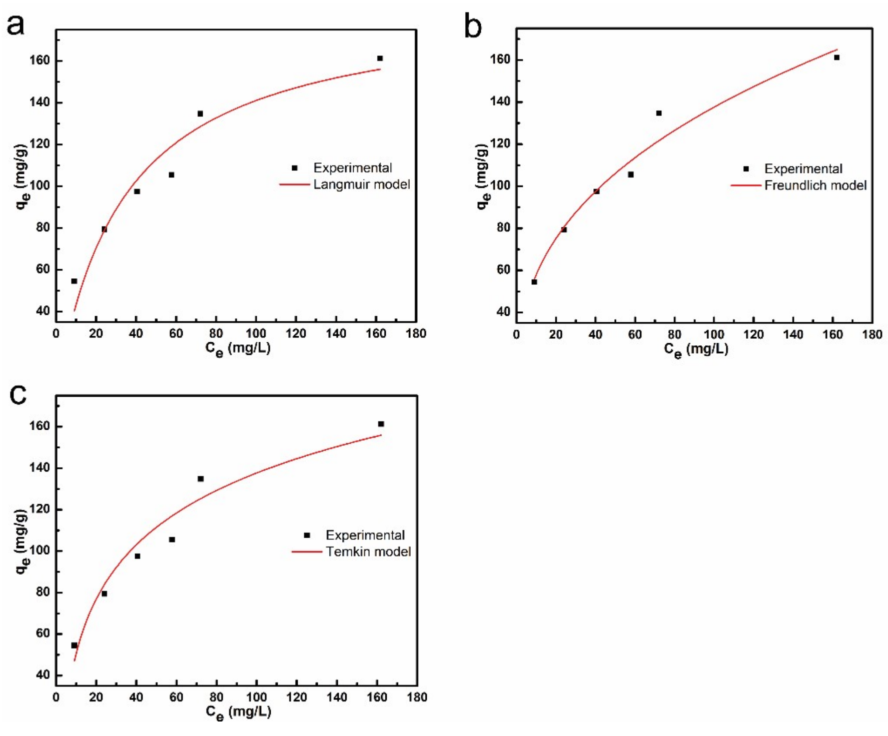

Fig. S4. Adsorption isotherms of Pd(II) on SPCM-2. a) Langmuir model, b) Freundlich model, c) Temkin model. ([sorbent] = 200 mg/L, Pd(II) = 20~200 mg/L, [HNO_3] = 1 M, T = 35 °C).

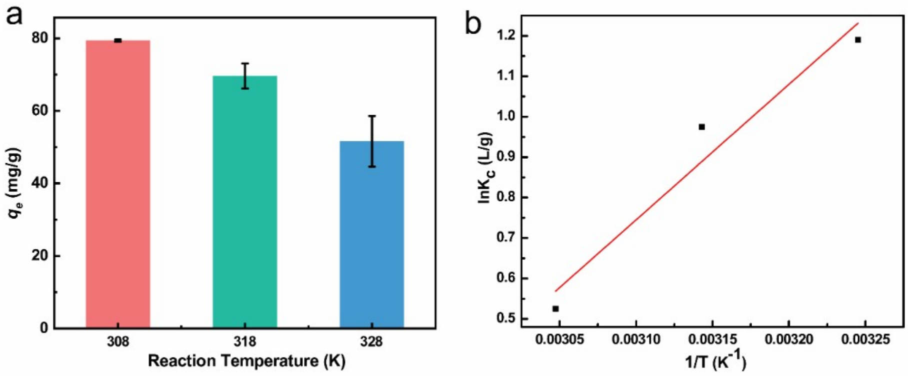

Fig. S5. a) Adsorption capacity of Pd(II) on the S-functionalized porous carbon sphere (SPCM-2) at different temperatures and b) the corresponding Van’t Hoff plot of lnKd versus 1/T. ([sorbent] = 200 mg/L, Pd(II) = 40 mg/L, [HNO_3] = 1 M)

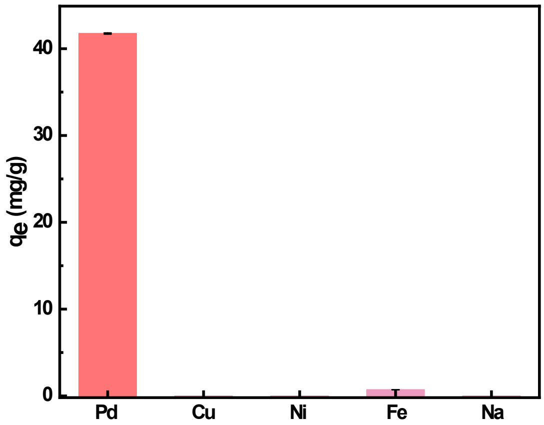

Fig. S6. Selective adsorption of Pd ions using the S-functionalized porous carbon sphere (SPCM-2) from actual industry acidic wastewater (pH=0.69) containing Pd, Cu, Ni, Fe and Na metal ions and surfactant. ([SPCM-2]=200 mg/L, T=35℃, $V_{solutin}$=50 mL)

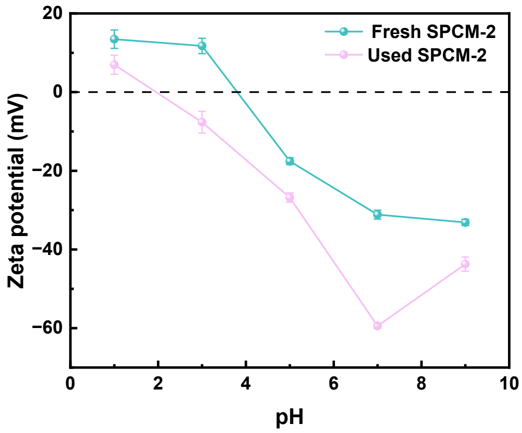

Fig. S7. pH-dependent zeta potential of the S-functionalized porous carbon sphere (SPCM-2) before and after Pd(II) adsorption.

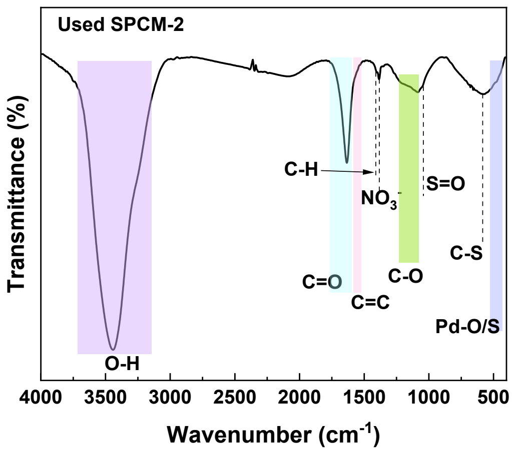

Fig. S8. FTIR spectrum of the used S-functionalized porous carbon sphere (SPCM-2) after Pd(II) adsorption.

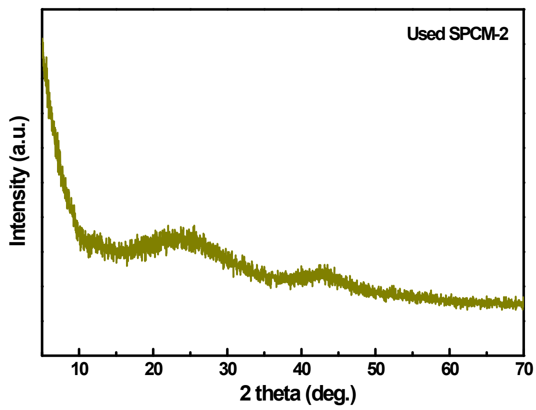

Fig. S9. XRD pattern of the used S-functionalized porous carbon sphere (SPCM-2) after Pd(II) adsorption.

Table S1. Concentrations of the ions in simulated spent fuel acidic wastewater, the distribution coefficients K_d and the selectivity coefficients K by the S-functionalized porous carbon sphere (SPCM-2).

Ions	Conc. (mg/L)	K_d (mL/g)			K		
		1 M	2 M	3 M	1 M	2 M	3 M
Pd	10.35	1.2×10^4	8.6×10^3	5.9×10^3	-	-	-
Ru	12.92	142.1	31.6	2.3	8.3×10^1	2.7×10^2	2.6×10^3
Te	13.36	113.5	24.6	12.7	1.0×10^2	3.5×10^2	4.6×10^2
Pb	14.55	91.2	40.9	38.1	1.3×10^2	2.1×10^2	1.5×10^2
Cu	13.70	93.7	6.2	0	1.3×10^2	1.4×10^3	$>5.9\times10^4$
Zn	13.16	91.9	0	0	1.3×10^2	$>8.6\times10^4$	$>5.9\times10^4$
Co	12.33	84.8	0	0	1.4×10^2	$>8.6\times10^4$	$>5.9\times10^4$
La	11.31	78.1	26.6	17.0	1.5×10^2	3.2×10^2	3.5×10^2
Ni	11.76	59.9	0	0	2.0×10^2	$>8.6\times10^4$	$>5.9\times10^4$
Ba	14.26	41.2	1.7	0	2.8×10^2	4.9×10^3	$>5.9\times10^4$
Nd	13.70	41.8	37.0	0	2.8×10^2	2.3×10^2	$>5.9\times10^4$
Cr	13.29	42.4	0	0	2.8×10^2	$>8.6\times10^4$	$>5.9\times10^4$
Cd	13.32	40.3	0	0	2.9×10^2	$>8.6\times10^4$	$>5.9\times10^4$
Mo	13.40	40.4	29.3	0	2.9×10^2	2.9×10^2	$>5.9\times10^4$
Ce	14.11	32.2	14.2	11.8	3.6×10^2	6.0×10^2	5.0×10^2
Zr	13.30	22.7	0	0	5.2×10^2	$>8.6\times10^4$	$>5.9\times10^4$
Mn	13.96	20.0	0	0	5.9×10^2	$>8.6\times10^4$	$>5.9\times10^4$
Nb	13.30	0	0	0	$>1.2\times10^5$	$>8.6\times10^4$	$>5.9\times10^4$
Fe	11.69	0	0	0	$>1.2\times10^5$	$>8.6\times10^4$	$>5.9\times10^4$
Ti	12.41	0	0	0	$>1.2\times10^5$	$>8.6\times10^4$	$>5.9\times10^4$
Ca	11.23	0	0	0	$>1.2\times10^5$	$>8.6\times10^4$	$>5.9\times10^4$
K	5.51	0	0	0	$>1.2\times10^5$	$>8.6\times10^4$	$>5.9\times10^4$
Al	13.96	0	0	0	$>1.2\times10^5$	$>8.6\times10^4$	$>5.9\times10^4$
Mg	12.56	0	0	0	$>1.2\times10^5$	$>8.6\times10^4$	$>5.9\times10^4$
Na	22.03	0	0	0	$>1.2\times10^5$	$>8.6\times10^4$	$>5.9\times10^4$
Li	13.67	0	0	0	$>1.2\times10^5$	$>8.6\times10^4$	$>5.9\times10^4$

Table S2. Specific surface area (SSA), average pore size, and pore volume of the as-prepared carbon samples.

Sample	Surface area*	Average pore size**	Pore volume**
	(m^2/g)	(nm)	(cm^3/g)
PCM	1104.5	1.62	0.367
SPCM-1	1227.1	2.41	0.682
SPCM-2	1496.5	2.02	0.901
SPCM-3	1316.4	2.49	0.788

*using Brunauer-Emmett-Teller (BET) method.

** using Horvath–Kawazoe (HK) method

Table S3. Kinetic parameters of Pd(II) adsorption on the S-functionalized porous carbon sphere (SPCM-2)*.

Kinetic Model	Parameters				
		PCM	SPCM-1	SPCM-2	SPCM-3
Pseudo-first-order model	k_1	0.008	0.0119	0.0123	0.0141
	q_e	2.808	2.7836	3.042	3.770
	R^2	0.7747	0.6739	0.6414	0.6764
Pseudo-second-order model	k_2	0.00117	0.000201	0.000156	0.000171
	q_e	29.214	70.522	80.128	76.394
	R^2	0.99895	0.99998	0.99995	0.99988
Intra-particle diffusion model	k_{i1}	6.107	19.318	21.171	17.690
	C_1	0.351	1.766	1.550	0.498
	R_1^2	0.9889	0.9716	0.9816	0.9972
	k_{i2}	0.972	1.275	1.808	2.255
	C_2	15.978	56.689	60.705	49.910
	R_2^2	0.9892	0.8673	0.9528	0.9586
	k_{i3}	0.187	0.0757	0.0400	0.171
	C_3	24.881	68.612	78.697	71.978
	R_3^2	0.5625	0.5675	0.3102	0.5822
Elovich model	α_E	132.301	2004644.551	145823.832	1715.729
	β_E	0.333	0.266	0.197	0.146
	R^2	0.9697	0.8390	0.8543	0.8962

*[sorbent] = 200 mg/L, Pd(II) = 40 mg/L, $[HNO_3]$ = 1 M, T = 35 °C

Table S4. Preparation cost of sorbent and their adsorption capacity for Pd (II) in HNO_3 solution

Sorbent \ HNO_3 (M) / q_e (mg/g)	Cost/g $	≤ 0.1	0.5	1	2	3	4	6	Ref.
CA-MP@SiO_2-P	284.2	-	-	-	-	24.5	-	-	1
CA-BOPhen@SiO_2-P	297.5	-	-	-	-	35.1	-	-	1
SBA-15-TEPA	16.24	pH=1.5 89.95	-	-	-	-	-	-	2
SiAaC	0.1372	pH=2 121.8	-	-	-	-	-	-	3
NTAamide(C8)/SiO_2-P	599.76	-	-	17	-	-	-	-	4
COP-2	120.82	-	-	182	-	-	-	-	5
CN-DAPhen	516.32	pH=1 124.1	-	-	-	-	-	-	6
C_8-Cyclen/CG-71M	560.42	-	-	73.7	-	-	-	-	7
KNiHC/SiO_2	4.984	pH=1 50.1	-	-		41.9	-	-	8
HEMAP/SiO_2-P	185.78	-	-	303.6	-		-	-	9
Tp-Azo-COF/SiO_2	108.22	-	-	-	-	88.5	-	-	10
CPTPN-Cl	470.96	-	-	-	-	102	-	-	11
Si-TpAL	106.4	-	-	47.9	-		-	-	12
isoPentyl-BTBP/SiO_2-P	96.46	-	-	-	-	26	-	-	13
MBI/XAD7HP	0.602	-	126.2	-	-		-	-	14
MBT/XAD7HP	0.602	-	137.6	-	-		-	-	14
MBO/XAD7HP	0.602	-	98.4	-	-		-	-	14
SBA-IL	18.48	pH=4 263	-	-	-		-	-	15
$KAlFe(CN)_6/SiO_2$	1.169	-	-	-	-	20.6	-	-	16
Si@-UiO−SO_3H MOF	76.16	-	-	6.4	-		-	-	17
P5COP-m-BPT	317.8	-	-	-	-	403	-	-	18
CTF-S	38.22	0.1 178.8	-	-	-	146.8	-	113.83	19
CTF-L	32.34	0.1 156.8	-	-	-	107.13	-	91.98	19
DHTH-FTD	230.72	pH=1 250	-	-	-	-	-	-	20
DMTH-FTD	94.92	pH=1 175	-	-	-	-	-	-	20
SPCM-2	0.02	pH=1 140.3 pH=2 156.1 pH=3 164.2	138.7	79.3	54.7	37.1	27	10.2	This work

Table S5. Parameters of isothermal model for adsorption of Pd(II) on the S-functionalized porous carbon sphere (SPCM-2).

Adsorption Isotherm	Parameters		
Langmuir	q_{max}	k_L	R^2
	188	0.0299	0.917
Freundlich	n	k_F	R^2
	2.67	24.5	0.961
Temkin	b	k_T	R^2
	67.8	0.382	0.938

Table S6. Thermodynamic parameters for adsorption of Pd(II) on the S-functionalized porous carbon sphere (SPCM-2) at different temperatures.

Temperature (K)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/(mol·K))
308	-3.05		
318	-2.58	-27.8	-80.1
328	-1.43		

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