Dioxins from the Sintering Process. (VII) Adsorption/Desorption data from 'de novo' Tests. Activation energy of (presumed) equilibrium values.

A.Buekens, P.Prakhar, L.Stieglitz*, P.Jacobs**

Vrije Universiteit Brussel, CHIS 2, Pleinlaan 2, B-1050 Brussels, Belgium
Forschungszentrum Karlsruhe, Karlsruhe, Germany
** Center for Surface Chemistry & Catalysis, K.U.L., Louvain, Belgium

Introduction.
Particulate can be analysed for its content of PCDD/F, PCBz, PCPh, PCB, PAH, … and eventually subjected to a standard 'de novo test', in which it is exposed for 2 hours to a stream of moist air at 300°C. After exposure it is analysed anew for its (new) content of PCDD/F, PCBz, PCPh, PCB, PAH, … Distinction is made thereby between the amount remaining on the thermally treated particulate and that reporting to the vapour phase (column c) .

Materials and Methods
Fly-ash from field 2 of the electrofilter thus was exposed to air for 2 hours, but the temperature was varied systematically, with a test at 200, 250, 300, 350, and 400°C. At each temperature the ratio of amount adsorbed to the solid to the amount volatilised to the gas phase was determined for the various isomer groups. Assuming that this partition is a consequence of establishing a desorption/adsorption equilibrium an activation energy for this equilibrium was derived this way for the various isomer groups.

Results and Discussion
Table 1a gives the PCDD values for both solid and gas phases for PCDD, Table 1 b gives the same data for PCDF, Table 1 c for their ratio. As expected the ratio (amount in the solid phase to the amount in the gas phase) decreases with rising temperature and increases with increasing chlorination level of the isomer group. Also PCDD are less volatile than PCDF. Arrhenius plots are thereby generated for the various congeners. The results are then used to determine activation energies.
Table 2 gives the numerical values for the adsorption energy derived by this method, together with the standard deviation and R2-value.
A similar exercise was made for 4 other samples, namely sintering belt feedmix, dust from field 3 of the electrofilter and, for the sake of comparison, dust settled from cement kiln off-gas and field 4 of the E-filter treating this gas. For each of these samples values at two different temperature levels were available. The results are given in Table 3.
Comments : all values at 200 and at 300 °C are above the best fitting straight line. Similarly the value for 250°C is always low. Visual inspection shows that a better fit results if the 250°C values were considered as an outlier.

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Table 1a PCDD Distribution in Solid and Gas Phases (ng/g)										
	TCDD final conc.		PeCDD final conc.		HxCDD final conc.		HpCDD final conc.		OCDD final conc.	
T (deg C)	Solid	Gas	Solid	Gas	Solid	Gas	Solid	Gas	Solid	Gas
200	1.740	4.050	5.970	4.850	11.700	2.350	13.400	0.940	9.430	0.520
250	8.610	322.000	29.500	618.000	47.700	326.000	36.200	95.700	16.600	14.500
300	53.200	415.000	116.000	625.000	114.000	325.000	72.600	98.900	34.600	11.900
350	10.700	291.000	23.400	867.000	23.400	517.000	17.900	170.000	17.900	27.000
400	0.540	99.800	0.750	70.600	0.560	28.100	0.340	10.100	0.370	0.000
INITIAL Conc.		1.930		6.980		13.500		14.500		10.300

Table 1b PCDF Distribution in Solid and Gas Phases (ng/g)										
	TCDF final conc.		PeDF final conc.		HxDF final conc.		HpDF final conc.		OCDF final conc.	
T (degC)	Solid	Gas	Solid	Gas	Solid	Gas	Solid	Gas	Solid	Gas
200	14.900	56.500	19.800	21.400	19.200	8.050	8.260	1.130	2.900	0.620
250	77.800	6389.000	65.900	3489.000	40.100	1067.000	12.400	128.000	4.630	7.920
300	785.000	6219.000	664.000	3299.000	344.000	1044.000	85.400	129.000	9.900	11.900
350	219.000	9972.000	199.000	5177.000	142.000	1786.000	57.600	249.000	5.770	12.100
400	9.900	1512.000	5.770	566.000	3.180	103.000	1.400	17.800	0.260	1.510
INITIAL Conc.		20.300		27.900		23.800		9.710		3.070

Table 1c Ratio of Dioxines (Solid phase/Gas phase)										
1E4/(T+273.16)	TCDD	PeCDD	HxCDD	HpCDD	OCDD	TCDF	PeCDF	HxCDF	HpCDF	OCDF
21.142	0.430	1.231	4.979	14.255	18.135	0.264	0.925	2.385	7.310	4.677
19.120	0.027	0.048	0.146	0.378	1.145	0.012	0.019	0.038	0.097	0.585
17.452	0.128	0.186	0.351	0.734	2.908	0.126	0.201	0.330	0.662	0.832
16.051	0.037	0.027	0.045	0.105	0.663	0.022	0.038	0.080	0.231	0.477
14.859	0.005	0.011	0.020	0.034		0.007	0.010	0.031	0.079	0.172

Table 2 Energies, Square-Correlation for PCDD/Fs										
	TCDD	PeCDD	HxCDD	HpCDD	OCDD	TCDF	PeCDF	HxCDF	HpCDF	OCDF
Eads(kcal/mole)	-6.7649	-10.5988	-13.4583	-14.2895	-9.4116	-6.2479	-8.6858	-9.7000	-10.3045	-7.0314
Square Correlation	0.6352	0.7555	0.8422	0.8725	0.6738	0.4663	0.5223	0.5144	0.5316	0.8244
Standard Deviation	2.6895									

Table 3 Results for samples EU1,EU2, EU3, EU4										
EU1	TCDD	PeCDD	HxCDD	HpCDD	OCDD	TCDF	PeCDF	HxCDF	HpCDF	OCDF
ln Ko					-15.117		-17.099	-15.04	-7.538	-2.1038
ko					2.7213E-07		3.75E-08	2.93908E-07	0.0005325	0.121992
slope'm'					0.9625		1.0481	0.9349	0.5087	0.1419
Eads(kcal/mole)					-19.139474		-20.841644	-18.590643	-10.11558	-2.8217053
EU2	TCDD	PeCDD	HxCDD	HpCDD	OCDD	TCDF	PeCDF	HxCDF	HpCDF	OCDF
ln Ko	-49.189	-56.29	-49.316	-44.763	-44.249	-53.006	-51.554	-49.047	-46.4	-32.941
ko	4.33999E-22	3.58E-25	3.82E-22	3.63E-20	6.066E-20	9.545E-24	4.077E-23	5.00217E-22	7.059E-21	4.942E-15
slope'm'	3.0763	3.4841	3.1097	2.8641	2.9124	3.3231	3.2474	3.1064	2.9857	2.2176
Eads(kcal/mole)	-61.17274067	-69.2819	-61.8369	-56.9531	-57.913562	-66.0804	-64.575093	-61.7712842	-59.37114	-44.097347
EU3	TCDD	PeCDD	HxCDD	HpCDD	OCDD	TCDF	PeCDF	HxCDF	HpCDF	OCDF
ln Ko				-4.6058	-5.6668	1.0362	7.358	0.6598	-5.845	-5.0676
ko				0.009994	0.00345892	2.818484	1568.696	1.934405415	0.0028943	0.0062975
slope'm'				0.338	0.3749	-0.0285	-0.0148	0.0024	0.3801	0.3163
Eads(kcal/mole)				-6.72119	-7.4549493	0.5667273	0.2943005	-0.0477244	-7.558352	-6.2896785
EU4	TCDD	PeCDD	HxCDD	HpCDD	OCDD	TCDF	PeCDF	HxCDF	HpCDF	OCDF
ln Ko	-7.2105			-12.428	-7.2105		-21.295	-12.968	-6.4754	-4.8897
ko										
slope'm'	0.5608			0.7921	0.5608		1.2314	0.8041	0.4682	0.345
Eads(kcal/mole)	-11.15160191			-15.751	-11.151602		-24.486595	-15.9896632	-9.310235	-6.8603828