Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

APPENDIX A

A STATISTICAL MECHANICAL MODEL FOR THERMODYNAMIC CORRECTION FACTOR

We present a statistical mechanical model for Eq.* MERGEFORMAT (19). We start by writing the microscopic definition of the chemical potential.

$$\mu = k_B T \ln\left(N \frac{\int dR^{N-1} e^{-\beta U(R^{N-1})}}{\int dR^N e^{-\beta U(R^N)}} \Lambda^3 \right) \tag{A1}$$

where U is the total potential energy function of the system, Λ is the thermal wave length, and R^N denotes the full set of molecular coordinate of an N particle system. The factor $\beta = 1/k_B T$ with k_B being the Boltzmann constant. Then, by inverting Eq. 5 we obtain

$$a = v^* N \frac{\int dR^{N-1} e^{-\beta U(R^{N-1})}}{\int dR^N e^{-\beta U(R^N)}} \tag{A2}$$

where the dependency on μ^0 and Λ have been adsorbed into the constant $v^* = \exp(-\beta\mu^0)\Lambda^3$. For an ideal gas $U = 0$, and therefore

$$\mu = k_B T \ln\left(\frac{N\Lambda^3}{V} \right) = k_B T \ln\left(\beta P \Lambda^3 \right), \quad a = v^* N / V = v^* \beta P \tag{A3}$$

where we used the ideal gas law on the form $PV = Nk_B T$. For the adsorbed layer we now consider two approximate models. The simplest model, the one obeying Henry's law, implies that adsorption is proportional to the gas pressure. The model describing this assumes that each molecule that adsorbs reduces the total energy by adsorption energy E_a irrespective of the occupancy of the surface. In other words, in the adsorption layer $U = -NE_a$ which gives

$$\mu = -E_a + k_B T \ln\left(C^s \Lambda^3 \right), \quad a = v^* C^s e^{-\beta E_a} \tag{A4}$$

with $C^s = N / V$ where N and V are the number in and volume of the surface layer.

The second model is the Langmuir model where particles are adsorbed on vacancy sites that can only be singly occupied. As derived in ref 7, the chemical potential and activity of this model is given by

$$\mu = -E_a + k_B T \ln\left[\frac{\theta}{(1-\theta)}\frac{\Lambda^3}{V_{\text{vac}}}\right], a = v^* \frac{e^{-\beta E_a}}{V_{\text{vac}}}\frac{\theta}{(1-\theta)} \tag{A5}$$

where V_{vac} is the volume of the vacancy pocket. Now, since the activity $a = \gamma C^s / C^{s,0}$. with the standard state concentration $C^{s,0}$ corresponding to the concentration of maximum occupancy, we can write the activity coefficient $\gamma = a / \theta$ or for both cases:

$$\gamma = v^* C^{s,0} e^{-\beta E_a} \qquad \text{Henry} \tag{A6}$$

$$\gamma = \frac{v^* e^{-\beta E_a}}{V_{\text{vac}}(1-\theta)} \qquad \text{Langmuir}$$

Now, let us consider Γ of the adsorption layer that is in contact with a gas

$$\Gamma = \frac{\langle N \rangle}{\langle N^2 \rangle - \langle N \rangle^2} \tag{A7}$$

where the grand canonical ensemble average is defined as

$$\langle \ldots \rangle = \frac{\sum_{N=0}^{\infty} \int \ldots \rho(R^N) dR^N}{\sum_{N=0}^{\infty} \int \rho(R^N) dR^N} \tag{A8}$$

with the probability distribution $\rho(R^N) \propto e^{-\beta W(R^N)} e^{\beta \mu N} / N! \propto e^{-\beta W(R^N)} (\beta P)^N / N!$. This implies for the Henry model that

$$\langle N \rangle = \frac{\sum_N N (V e^{\beta E_{\text{ads}}} \beta P)^N / N!}{\sum_N (V e^{\beta E_{\text{ads}}} \beta P)^N / N!} = V e^{\beta E_{\text{ads}}} \beta P \tag{A9}$$

$$\langle N^2 \rangle = \frac{\sum_N N^2 (V e^{\beta E_{\text{ads}}} \beta P)^N / N!}{\sum_N (V e^{\beta E_{\text{ads}}} \beta P)^N / N!} = V e^{\beta E_{\text{ads}}} \beta P (V e^{\beta E_{\text{ads}}} \beta P + 1)$$

Where we used $\sum_N x^N / N! = \exp(x)$, $\sum_N N x^N / N! = x \exp(x)$, and $\sum_N N^2 x^N / N! = x(x+1)\exp(x)$. We used P for the gas pressure while V and N are properties of the adsorption layer. By introducing these expressions into the relation A7 we obtain

$$\Gamma = \frac{V e^{\beta E_{\text{ads}}} C}{V e^{\beta E_{\text{ads}}} C (V e^{\beta E_{\text{ads}}} C + 1) - (V e^{\beta E_{\text{ads}}} C)^2} = 1 \qquad \text{Henry} \tag{A10}$$

This is expected from Eq. * MERGEFORMAT (19). For the Langmuir model, we replace the integral by $V_{\text{vac}}^{N} M(M-1)...(M-N+1)$ as in ref 7. Then, by using the definition of the binomial coefficients we can write

$$\langle N \rangle = \frac{\sum_N N \binom{M}{N} (V_{\text{vac}} e^{\beta E_{\text{ads}}} \beta P)^N}{\sum_N \binom{M}{N} (V_{\text{vac}} e^{\beta E_{\text{ads}}} \beta P)^N} = \frac{M V_{\text{vac}} e^{\beta E_{\text{ads}}} \beta P}{V_{\text{vac}} e^{\beta E_{\text{ads}}} \beta P + 1} \tag{A11}$$

$$\langle N^2 \rangle = \frac{\sum_N N^2 \binom{M}{N} (V_{\text{vac}} e^{\beta E_{\text{ads}}} \beta P)^N}{\sum_N \binom{M}{N} (V_{\text{vac}} e^{\beta E_{\text{ads}}} \beta P)^N} = \frac{M V_{\text{vac}} e^{\beta E_{\text{ads}}} \beta P (M V_{\text{vac}} e^{\beta E_{\text{ads}}} \beta P + 1)}{(V_{\text{vac}} e^{\beta E_{\text{ads}}} \beta P + 1)^2}$$

Here we used $\sum_N \binom{M}{N} x^N = (x+1)^M$, $\sum_N \binom{M}{N} N x^N = Mx(x+1)^{M-1}$, and $\sum_N \binom{M}{N} N^2 x^N = Mx(x+1)^{M-2}(xM+1)$

By introducing these expressions, we obtain

$$\Gamma = V_{\text{vac}} e^{\beta E_{\text{ads}}} \beta P + 1 \qquad \text{Langmuir} \tag{A12}$$

We can relate this to the Langmuir constant as $K_{i,g}^{L} = V_{\text{vac}} e^{\beta E_{\text{ads}}} \beta$ which gives

$$\Gamma = K_{i,g}^{L} P + 1 \tag{A13}$$

Finally, by substitution of the inverse Langmuir equation $P = \theta / K_{i,g}^{L}(1-\theta)$ we end up at Eq. * MERGEFORMAT (19).

APPENDIX B

LANGMUIR AND HENRY EQUILIBRIUM CONSTANTS FROM SIMULATION DATA

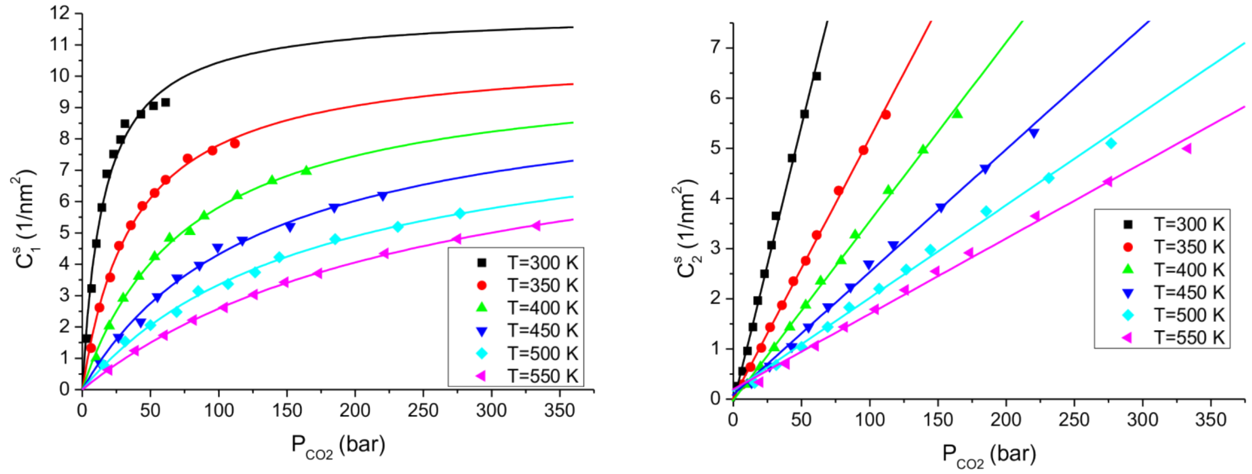

Figure S1. Adsorption isotherm of the first (a) and second layer (b) as funciton of pressure at different temperatures. The straigh lines are fitted with Langmuir (layer 1) and Henry (layer 2) isotherms.

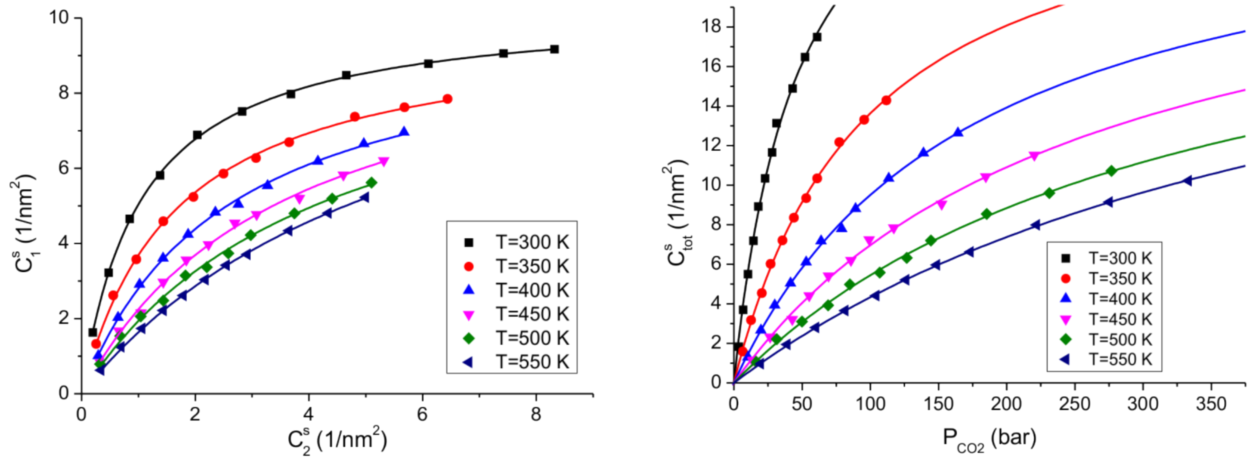

Figure S2. Adsorption isotherms valid for the first and second layers (a), and for the total layer and the gas (b) at different temperatures. The straight line is obtained from fits with a Langmuir isotherm .

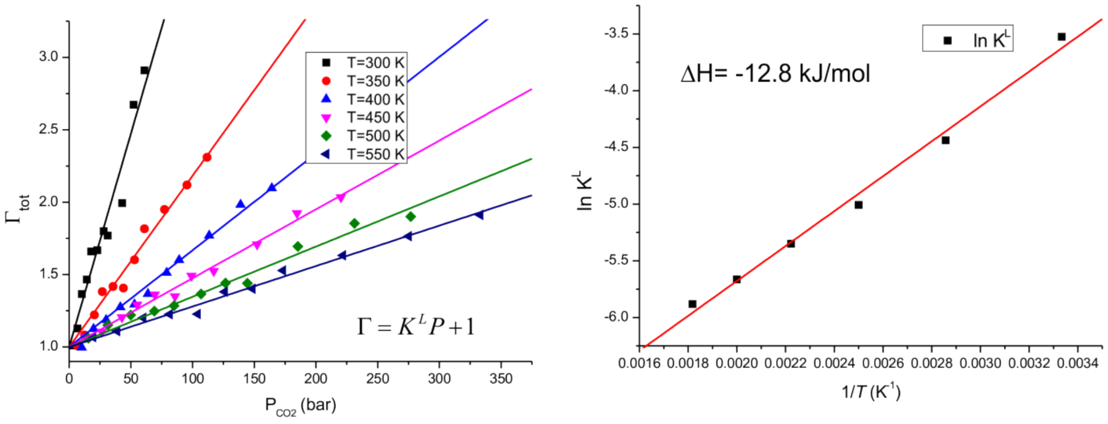

Figure S3. Thermodynamic correction factors for CO_2 adsorbed on a graphite surface as a function of gas pressure at different temperatures (a). The slope of the fitted line is the Langmuir constant (see Appendix, equation A13). (b) The linear fit of the natural logarithm of the Langmuir constant to the inverse temperature, gives the energy of adsorption. The value $-E_{ads}$= ΔH = -12.8 kJ/mol from the slope.