

# Prediction of gas adsorption selectivity by ideal adsorption solution theory (IAST)

by Michael J. Bojdys

URL: <http://mjbojdys.blogspot.com/>



This work is licensed under a Creative Commons Attribution-ShareAlike 3.0 Unported License.

URL: <http://creativecommons.org/licenses/by-sa/3.0/>

Ideal adsorption solution theory (IAST) fitting and analysis was performed using *Mathematica 9.0* and *Microsoft Excel* graphing and data analysis software. The following manual will guide you through the creation of a *Mathematica* notebook (\*.nb) file for computational purposes only. The underlying theory is explained elsewhere [Myers, A. L. and Prausnitz, J. M. *AIChE J.*, **1965**, *11*, 121-127]. The analysis is based on [Herm, Z. R. *et al. J. Am. Chem. Soc.* **2011**, *133*, 5664–5667], and special thanks go to Zoey R. Herm for helpful discussions and for providing the *Microsoft Excel* template (*IAST\_spreadsheet\_KrXe.xlsx*).

## Import of gas sorption data.

Gas Sorption Analysis was performed on a Micromeritics ASAP 2420 volumetric sorption analyser equipped with a chiller circulator. Gases analysed in this example were krypton (Kr) and xenon (Xe) at 298 K. Data is stored in the folder *C:\IAST\_example\* in \*.csv format, and is provided in terms of Absolute Pressure (in mbar) and Quantity Adsorbed (in mmol/g), with the first line of the file containing the header information. We define two variables *Krdata* and *Xedata* for the adsorption branch of the Kr- and Xe-isotherms, respectively.

```
Krdata = Import["C:\IAST_example\298K_Kr.csv", "HeaderLines" -> 1]
{{0, 0}, {0.00363933, 0.00502156}, {0.00758546, 0.0104549}, {0.0101257, 0.0141691}, {0.0138378, 0.0192323},
{0.0266871, 0.0363951}, {0.0403837, 0.0543981}, {0.0668121, 0.0876943}, {0.107604, 0.137322}, {0.148009, 0.184615},
{0.22829, 0.275387}, {0.309752, 0.361249}, {0.390505, 0.442966}, {0.471674, 0.519098}, {0.552466, 0.590545},
{0.633384, 0.658472}, {0.714283, 0.724704}, {0.795324, 0.786113}, {0.876094, 0.844948}, {0.926798, 0.88037}, {1.00666, 0.933718}}

Xedata = Import["C:\IAST_example\298K_Xe.csv", "HeaderLines" -> 1]
{{0, 0}, {0.00316771, 0.0569117}, {0.00698778, 0.123686}, {0.0100666, 0.176238}, {0.013563, 0.233115}, {0.0265964, 0.432984}, {0.0406218, 0.622286},
{0.0671493, 0.917811}, {0.108487, 1.25094}, {0.146931, 1.46705}, {0.22784, 1.75763}, {0.307935, 1.93391}, {0.408988, 2.07715}, {0.491657, 2.16105},
{0.573381, 2.22555}, {0.655048, 2.27645}, {0.736322, 2.32012}, {0.817573, 2.35661}, {0.898829, 2.38913}, {0.948114, 2.40798}, {1.01655, 2.43043}}
```

## Parameterisation of the Freundlich-Langmuir equation for dual-site adsorption.

IAST estimations were performed using the dual-site Langmuir-Freundlich fits of the single-component isotherms. In equation (1),  $p$  is the pressure of the bulk gas at equilibrium with the adsorbed phase (in mbar),  $q$  is the adsorbed amount per mass of adsorbent (in mmol/g),  $q(m,1)$  and  $q(m,2)$  are the saturation capacities of sites 1 and 2 (in mmol/g),  $b1$  and  $b2$  are the affinity coefficients of sites 1 and 2 (in 1/mbar), and  $n1$  and  $n2$  represent the deviations from an ideal, homogeneous surface.

$$q = \frac{q_{m,1} b_1 p^{1/n_1}}{1 + b_1 p^{1/n_1}} + \frac{q_{m,2} b_2 p^{1/n_2}}{1 + b_2 p^{1/n_2}} \quad (1)$$

The adsorption selectivity,  $S$ , for binary mixtures of components 1 and 2 is defined as:

$$S = \frac{q_1/q_2}{p_1/p_2} \quad (2)$$

where  $q_1$  and  $q_2$  are the molar loadings (in mmol/g) and  $p_1$  and  $p_2$  are the partial pressures of species 1 and 2 (in mbar), respectively.

IAST is analogous to Raoult's law and assumes an ideal solution of the gas components 1 and 2 at equilibrium, i.e. the conditions for IAST are:

$$xp_{total} = yp_1 \quad (3)$$

and

$$(1-x)p_{total} = (1-y)p_2 \quad (4)$$

where  $x$  is the molar fraction of constituent 1 in the gas phase and  $y$  is the molar fraction of adsorbed constituent 1.  $p_{total}$ ,  $p_1$  and  $p_2$  are the total pressure and the pressure of constituents 1 and 2, respectively.

Pressure  $p_1$  and  $p_2$  of constituents 1 and 2 correspond to the spreading pressure  $p_{spread}$  of the binary mixture of constituents 1 and 2, and is given by:

$$\frac{Ap_{spread}}{RT} = \int_0^{p_i^0} \frac{q_i}{p_i} dp_i = q_{total} \ln \left( 1 + \sum_{i=0}^N b_i p_i \right) \quad (5)$$

where  $A$ ,  $R$ ,  $T$  and  $q_i$  are the specific surface area of the adsorbent, gas constant, temperature and the adsorbed amount of constituent  $i$  at pressure  $p_0(i)$ . At equilibrium equation (5) will be the same for  $i = 1$  and 2, hence:

$$q_{total,1} \ln \left( \frac{1 + b_1 p_{total} y}{x} \right) - q_{total,2} \ln \left( \frac{1 + b_2 p_{total} (1-y)}{(1-x)} \right) = 0 \quad (6)$$

In simpler terms, we need to find a mathematical description for real gas sorption data in terms of equation (1), then find the integral of this mathematical description to arrive at the equivalent of equation (5), and then to solve for the equilibrium condition outlined in equation (6).

To that end, we define the variable  $FL_{model}$  which depends on four parameters  $q_1$ ,  $b_1$ ,  $q_2$  and  $b_2$  and the variable  $x$ . The parameters  $n_1$  and  $n_2$  are set to 1 for simplicity, assuming for ideal of adsorption surfaces.

$$FL_{model} = \left( \frac{q_1 \cdot b_1 \cdot (x^{1/n_1})}{1 + b_1 \cdot (x^{1/n_1})} \right) + \left( \frac{q_2 \cdot b_2 \cdot (x^{1/n_2})}{1 + b_2 \cdot (x^{1/n_2})} \right)$$

$$\frac{b_1 q_1 x^{\frac{1}{n_1}}}{1 + b_1 x^{\frac{1}{n_1}}} + \frac{b_2 q_2 x^{\frac{1}{n_2}}}{1 + b_2 x^{\frac{1}{n_2}}}$$

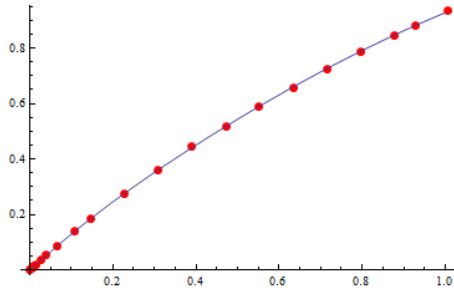
## Nonlinear curve fitting using gas sorption data.

```
Krfit = FindFit[Krdata, {FLmodel}, {q1, b1, n1, q2, b2, n2}, x, Method -> "PrincipalAxis", MaxIterations -> 200]
{q1 -> 0.344383, b1 -> 0.970567, n1 -> 0.386091, q2 -> 1.5515, b2 -> 0.955002, n2 -> 0.97502}
```

```
Xefit = FindFit[Xedata, {FLmodel}, {q1, b1, n1, q2, b2, n2}, x, Method -> "PrincipalAxis", MaxIterations -> 200]
{q1 -> 1.17808, b1 -> 0.91514, n1 -> 1.65216, q2 -> 1.97641, b2 -> 16.0372, n2 -> 0.822391}
```

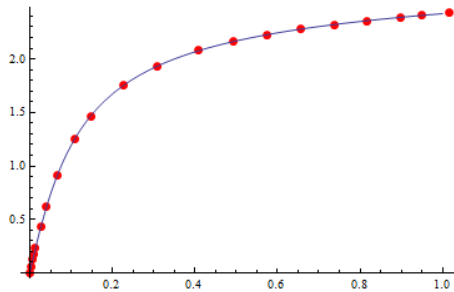
## Plot of gas sorption data and the dual-site Freundlich-Langmuir fit for Kr (at 298 K).

```
Show[ListPlot[Krdata, PlotStyle -> {Red, PointSize[.02]}], Plot[FLmodel /. Krfit, {x, 0, 1}], PlotRange -> All, AxesOrigin -> {0, 0}]
```



## Plot of gas sorption data and the dual-site Freundlich-Langmuir fit for Xe (at 298 K).

```
Show[ListPlot[Xedata, PlotStyle -> {Red, PointSize[.02]}], Plot[FLmodel /. Xefit, {x, 0, 1}], PlotRange -> All, AxesOrigin -> {0, 0}]
```



**NOTE:** at this point the mathematical descriptions for both isotherms can be already used to calculate molar selectivities (useful in some instances).

## Finding the integrals.

```
Krint = Integrate[(FLmodel /. Krfit) / x, x]
```

```
0.12905 x2.59006 Hypergeometric2F1[1., 1., 2., -0.970567 x2.59006] - 1.44467 x1.02562 Hypergeometric2F1[1., 1., 2., -0.955002 x1.02562]
```

```
Xeint = Integrate[(FLmodel /. Xefit) / x, x]
```

```
1.78121 x0.605268 Hypergeometric2F1[1., 1., 2., -0.91514 x0.605268] - 26.0666 x1.21597 Hypergeometric2F1[1., 1., 2., -16.0372 x1.21597]
```

## Perform IAST.

```

Grid[
Table[
FindRoot[
(0.12904950030385282` (0.8 Q / (q))2.590063289209942` Hypergeometric2F1[0.9999999999999999`, 1., 2., -0.9705667980730204` (0.8 Q / (q))2.590063289209942`] +
1.4446695961090197` (0.8 Q / (q))1.0256200128453732` Hypergeometric2F1[1., 1., 2., -0.955001890792215` (0.8 Q / (q))1.0256200128453732`]) -
(0.12904950030385282` × 02.590063289209942` Hypergeometric2F1[0.9999999999999999`, 1., 2., -0.9705667980730204` 02.590063289209942`] +
1.4446695961090197` × 01.0256200128453732` Hypergeometric2F1[1., 1., 2., -0.955001890792215` 01.0256200128453732`]) =
(1.7812105112139922` (0.2 Q / (1 - q))0.6052683136519844` Hypergeometric2F1[1., 1., 2., -0.91514016262247` (0.2 Q / (1 - q))0.6052683136519844`] +
26.066580367681794` (0.2 Q / (1 - q))1.2159665138208258` Hypergeometric2F1[1., 1., 2., -16.03718705753503` (0.2 Q / (1 - q))1.2159665138208258`]) -
(1.7812105112139922` × 00.6052683136519844` Hypergeometric2F1[1., 1., 2., -0.91514016262247` 00.6052683136519844`] +
26.066580367681794` × 01.2159665138208258` Hypergeometric2F1[1., 1., 2., -16.03718705753503` 01.2159665138208258`]), {q, .99}], {Q, 0.1, 1, 0.1}]
q → 0.214832
q → 0.215519
q → 0.215141
q → 0.214132
q → 0.212488
q → 0.210418
q → 0.208113
q → 0.205705
q → 0.203272
q → 0.200863

```

At this point the resulting values for the partial pressure of Kr (i.e.  $q$ ) can be processed and visualised according to above equations in e.g. *Microsoft Excel* (c.f. *IAST\_spreadsheet\_KrXe.xlsx*).



This work is licensed under a Creative Commons Attribution-ShareAlike 3.0 Unported License.