adsorption_isotherm_fitting

Release v0.0.3

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CONTENTS:

CHAPTER

ONE

INSTALLATION

1.1 Docker

```
docker pull dejac001/isotherm-fitting-users:0.0.4
docker run -ti -v $PWD:/home/pyomo/shared/ dejac001/isotherm-fitting-users:0.0.4 #␣
↪run interactively inside container (ubuntu-based)
```

1.2 Singularity

```
module load singularity
singularity pull docker://dejac001/isotherm-fitting-users:0.0.4
mv isotherm-fitting-users_0.0.4.sif /path/to/shared/directory/isotherm-fitting-users_
↪0.0.4.sif
singularity exec -B $PWD:/home/pyomo/shared /path/to/shared/directory/isotherm-
↪fitting-users_0.0.4.sif python3 path/to/input/file.py
```

1.3 Scipy Only

```
pip3 install Pyomo chem-util matplotlib pandas numpy realgas>=1.0.2
python3 -m pip3 install https://github.com/dejac001/adsorption_isotherm_fitting/
↪archive/v0.0.5.tar.gz
```

CHAPTER

TWO

CO2/N2 UNARY EXAMPLE

In this example, we fit temperature-dependent unary data from [PXSL14].

2.1 Initialization

We first load the necessary packages

```
>>> import pyomo.environ as pyo
>>> import matplotlib.pyplot as plt
>>> import pandas as pd
>>> from isotherm_models.unaryisotherm import LangmuirUnary
```

2.2 CO2

We first get the data from the data file

```
>>> data = pd.read_csv('data_sets/CO2_BEA.csv')
```

Using pandas, we can easily take a peek at the data we have input from our .csv file

```
>>> data.head()
    P [atm]  Q [mmol/g]  T [K] adsorbate
0  0.029814    0.096491  273.0       CO2
1  0.055856    0.175439  273.0       CO2
2  0.109177    0.328947  273.0       CO2
3  0.246821    0.719298  273.0       CO2
4  0.313781    0.903509  273.0       CO2
```

Before solving the model, we convert the partial pressures to si units

```
>>> P_i = data['P [atm]']*101325  # convert to Pa -- si units
```

so that we can create the model

```
>>> co2_model = LangmuirUnary(P_i, data['Q [mmol/g]'], data['T [K]'], name='CO2')
```

and solve it

```
>>> co2_model.solve()
```

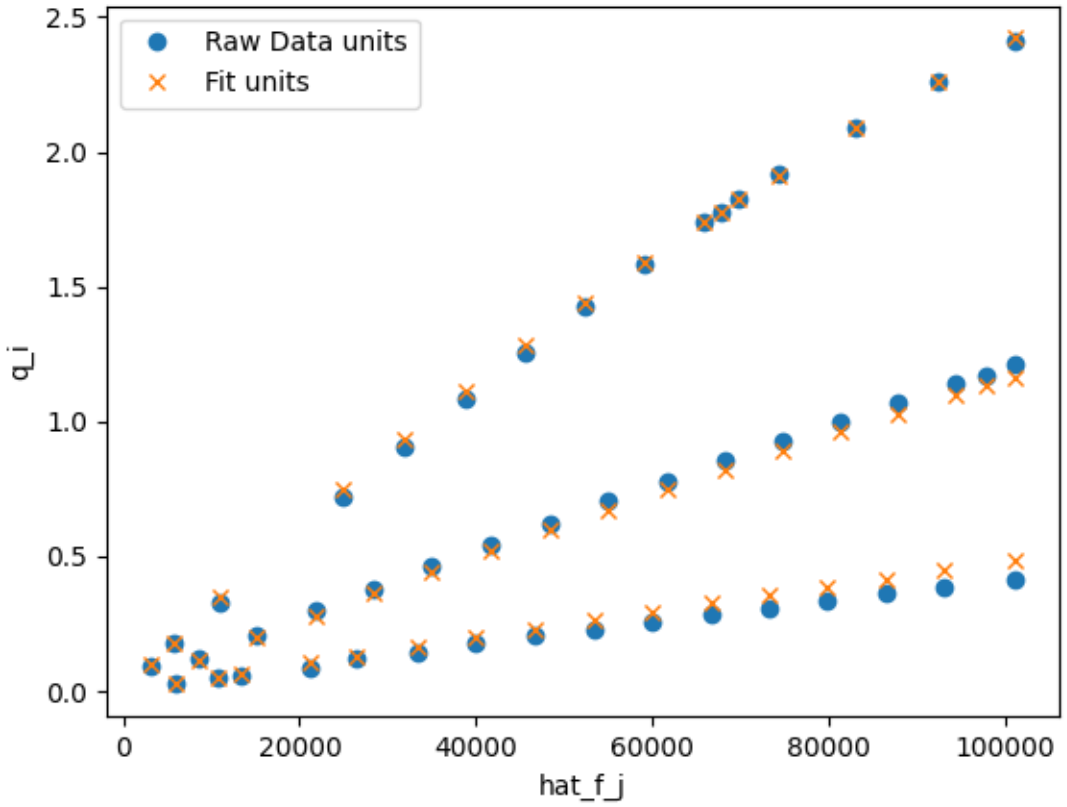
We then take a look at the results

```
>>> co2_model.get_R2_pyomo()
0.99796
>>> co2_model.get_objective()
0.007229102
>>> co2_model.dH_i.display()
dH_i : Size=1
    Key  : Value
    None : -20780.90809523844
>>> co2_model.q_mi.display()
q_mi : Size=1
    Key  : Value
    None : 8.95582798469325
>>> co2_model.k_i_inf.display()
k_i_inf : Size=1
    Key  : Value
    None : 3.8656918601559114e-10
```

And save the results to a file

```
>>> fig = plt.figure()
>>> fig, ax = co2_model.plot_unary(fig=fig)
>>> _ = ax.legend()
>>> fig.savefig('docs/source/CO2_example.png')
```

which looks like



2.3 N2

We repeat a similar approach for the N2 isotherms, first formatting the data for input to the model

```
>>> data = pd.read_csv('data_sets/N2_BEA.csv')
```

Using pandas, we can easily take a peek at the data we have input from our .csv file

```
>>> data.head()
    P [atm]  Q [mmol/g]  T [K] adsorbate
0  0.525470    0.070175  303.0        N2
1  0.592387    0.078947  303.0        N2
2  0.656824    0.083333  303.0        N2
3  0.722502    0.092105  303.0        N2
4  0.788179    0.100877  303.0        N2
```

Before solving the model, we convert the partial pressures to si units

```
>>> P_i = data['P [atm]']*101325  # convert to Pa -- si units
```

Instantiating (creating) the model

```
>>> n2_model = LangmuirUnary(P_i, data['Q [mmol/g]'], data['T [K]'], name='N2')
```

Solving it

```
>>> n2_model.solve()
```

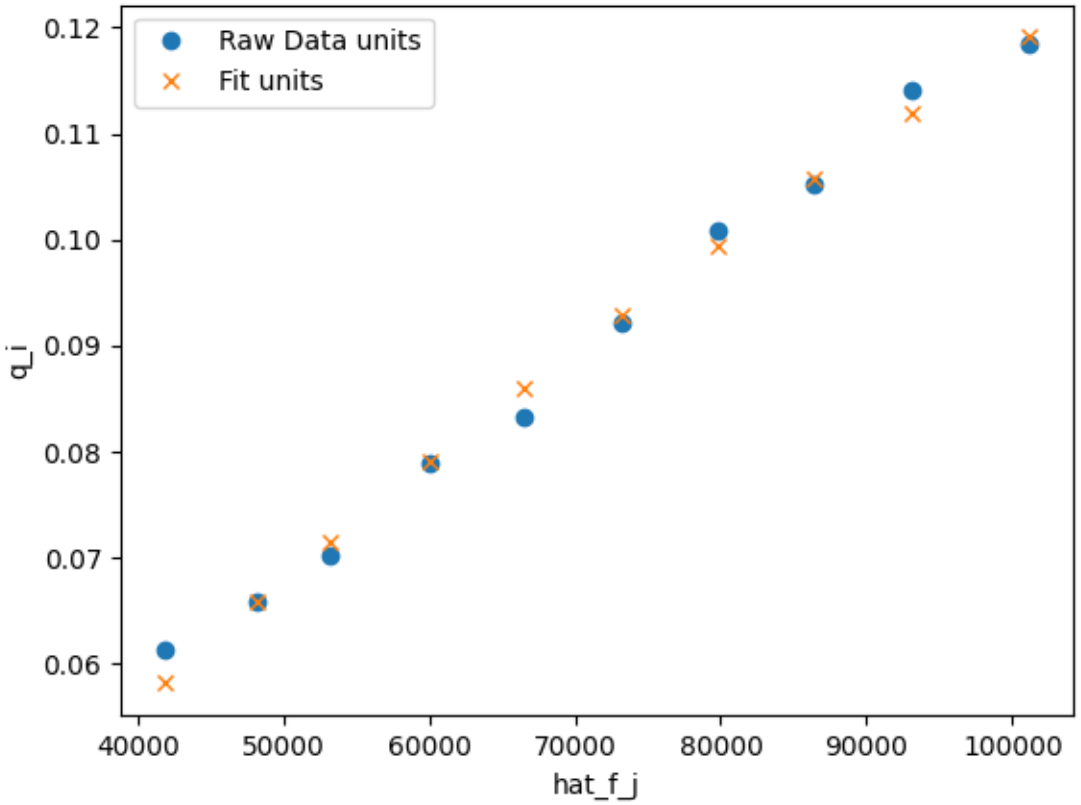
We then take a look at the results

```
>>> n2_model.get_R2_pyomo()
0.99262
>>> n2_model.get_objective()
0.00194249
>>> n2_model.dH_i.display()
dH_i : Size=1
    Key  : Value
    None : -12557.526993112784
>>> n2_model.q_mi.display()
q_mi : Size=1
    Key  : Value
    None : 0.45280441671269905
>>> n2_model.k_i_inf.display()
k_i_inf : Size=1
    Key  : Value
    None : 2.412336128388879e-08
```

And save the results to a file

```
>>> fig = plt.figure()
>>> fig, ax = n2_model.plot_unary(fig=fig)
>>> _ = ax.legend()
>>> fig.savefig('docs/source/N2_example.png')
```

which looks like



2.4 Comparison to scipy

```
>>> import numpy as np
>>> popt, pcov = co2_model.solve_scipy()
>>> popt
array([  3.71939309, -10.14817759,  -7.28715595])
>>> popt - np.array(list(map(pyo.value, [co2_model.q_mi_star, co2_model.A_i, co2_
↪model.H_i_star])))
array([3.28355311e-05, 3.67969745e-05, 3.88858220e-05])
```

CHAPTER

THREE

H2S/CH4 EXAMPLE

In this example, we fit temperature-dependent binary data from [STS15] and compare the results to using the extended Langmuir combining rule.

3.1 Initialization

First, we import the necessary packages

```
>>> import pyomo.environ as pyo
>>> import matplotlib.pyplot as plt
>>> import pandas as pd
>>> from isotherm_models.unaryisotherm import LangmuirUnary
>>> from isotherm_models.binaryisotherm import BinaryLangmuir
```

First, we grab the data for adsorption of H2S:

```
>>> df = pd.read_csv('data_sets/CH4_H2S_MFI_binary_with_fugacity.csv')
>>> hat_f_i, hat_f_j, q_i, T = df['fugacity H2S [Pa]'], df['fugacity CH4 [Pa]'], df[
↪'Q H2S [mmol/g]'], df['T [K]']
```

Here, we are going to fit the loading of H2S, `q_i`, as a function of the (mixture) fugacities of H2S, `hat_f_i`, and CH4, `hat_f_j`. Since the data file includes both binary and unary data (including CH4 unary data where H2S is not present), we need to find the data points where H2S is present. We can do this with a list comprehension as below

```
>>> all_points = [i for i in range(len(q_i)) if q_i[i] > 0.]
```

Now, we can create a model with all of these points. We choose the *isotherm_models.binaryisotherm.BinaryLangmuir* model.

```
>>> h2s_binary = BinaryLangmuir(
...     [hat_f_i[i] for i in all_points],
...     [hat_f_j[i] for i in all_points],
...     [q_i[i] for i in all_points],
...     [T[i] for i in all_points],
...     name='H2S_binary'
... )
```

Similarly, we can find the indices of points where *only* H2S is present (i.e., the unary points for H2S), using the following code

```
>>> unary_points = [i for i in range(len(q_i)) if hat_f_j[i] < 1e-12]
>>> f_i = [hat_f_i[i] for i in unary_points]
```

And we can create a unary model as

```
>>> h2s_unary = LangmuirUnary(
...     f_i,
...     [q_i[i] for i in unary_points],
...     [T[i] for i in unary_points],
...     name='H2S_unary'
... )
```

We can undertake a similar procedure for CH4, as below

```
>>> df = pd.read_csv('data_sets/CH4_H2S_MFI_binary_with_fugacity.csv')
>>> hat_f_i, hat_f_j, q_i, T = df['fugacity CH4 [Pa]'], df['fugacity H2S [Pa]'], df[
↪'Q CH4 [mmol/g]'], df['T [K]']
>>> all_points = [i for i in range(len(q_i)) if q_i[i] > 0.]
>>> unary_points = [i for i in range(len(q_i)) if hat_f_j[i] < 1e-12]
>>> f_i = [hat_f_i[i] for i in unary_points]
>>> ch4_unary = LangmuirUnary(f_i,
...     [q_i[i] for i in unary_points],
...     [T[i] for i in unary_points],
...     name='CH4_unary'
... )
>>> ch4_binary = BinaryLangmuir(
...     [hat_f_i[i] for i in all_points],
...     [hat_f_j[i] for i in all_points],
...     [q_i[i] for i in all_points],
...     [T[i] for i in all_points],
...     name='CH4_binary'
... )
```

3.2 Solution

We solve the ch4_unary model first

```
>>> ch4_unary.solve()
```

and observe that the fit is quite good.

```
>>> ch4_unary.get_R2_pyomo()
0.9998
>>> ch4_unary.get_objective()
0.0007123352658190
```

We can take a look at the final parameters that were obtained

```
>>> ch4_unary.dH_i.display()
dH_i : Size=1
    Key  : Value
    None : -20205.7398278234
```

```
>>> ch4_unary.q_mi.display()
q_mi : Size=1
    Key  : Value
    None : 2.7226241284913613
```

```
>>> ch4_unary.k_i_inf.display()
k_i_inf : Size=1
    Key  : Value
    None : 6.61203298602151e-10
```

Then we can do the same thing with the H2S unary model

```
>>> h2s_unary.solve()
>>> h2s_unary.get_R2_pyomo()
0.998700
>>> h2s_unary.get_objective()
0.0053414
```

Alternatively, we can display results at once

```
>>> h2s_unary.display_results()
R2 : Size=1
    Key  : Value
    None : 0.9987002690496689
objective : Size=1, Index=None, Active=True
    Key  : Active : Value
    None :   True : 0.0053414186202173485
H_i_star : Size=1, Index=None
    Key  : Lower : Value               : Upper : Fixed : Stale : Domain
    None :  None : -10.976064382768586 :  None : False : False :  Reals
A_i : Size=1, Index=None
    Key  : Lower : Value              : Upper : Fixed : Stale : Domain
    None :  None : -7.365904878303015 :  None : False : False :  Reals
q_mi_star : Size=1, Index=None
    Key  : Lower : Value              : Upper : Fixed : Stale : Domain
    None :  None : 1.0109486926682547 :  None : False : False :  Reals
q_mi : Size=1
    Key  : Value
    None : 3.1127110247255563
k_i_inf : Size=1
    Key  : Value
    None : 1.6091644633767268e-10
dH_i : Size=1
    Key  : Value
    None : -31300.464752469943
```

Before solving the binary models, it is useful to have a good initial guess. One option is to initialize the binary variables from the Langmuir combining rule

```
>>> h2s_binary.H_i_star = pyo.value(h2s_unary.H_i_star)
>>> h2s_binary.A_i = pyo.value(h2s_unary.A_i)
>>> h2s_binary.q_mi_star = pyo.value(h2s_unary.q_mi_star)
>>> h2s_binary.A_j = pyo.value(ch4_unary.A_i)
>>> h2s_binary.H_j_star = pyo.value(ch4_unary.H_i_star)
>>> ch4_binary.H_i_star = pyo.value(ch4_unary.H_i_star)
>>> ch4_binary.A_i = pyo.value(ch4_unary.A_i)
>>> ch4_binary.q_mi_star = pyo.value(ch4_unary.q_mi_star)
>>> ch4_binary.A_j = pyo.value(h2s_unary.A_i)
>>> ch4_binary.H_j_star = pyo.value(h2s_unary.H_i_star)
```

And then solve them using the usual syntax

```
>>> h2s_binary.solve()
>>> ch4_binary.solve()
>>> h2s_binary.get_R2_pyomo()
0.9988281256
>>> h2s_binary.get_objective()
0.0186995038
>>> ch4_binary.get_R2_pyomo()
0.999329631
>>> ch4_binary.get_objective()
0.007515807
```

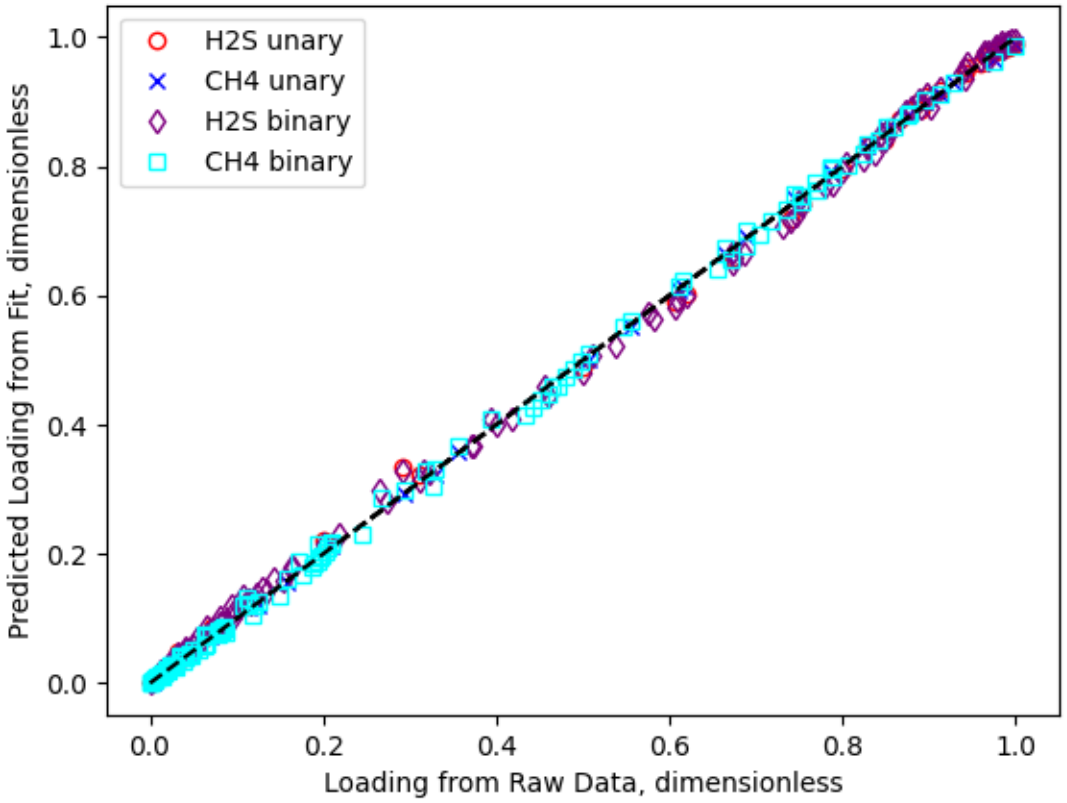
which demonstrates that the fits are again quite good. It is of interest to compare the binary fit parameters to the unary parameters

```
>>> pyo.value(h2s_binary.H_i_star)
-11.073113
>>> pyo.value(h2s_unary.H_i_star)
-10.97606
>>> pyo.value(h2s_binary.q_mi_star)
1.0189875
>>> pyo.value(h2s_unary.q_mi_star)
1.0109486
>>> pyo.value(h2s_binary.A_i)
-7.32572
>>> pyo.value(h2s_unary.A_i)
-7.36590
```

We can also plot all the results to a figure, and save it to a file

```
>>> fig = plt.figure()
>>> fig, ax = h2s_unary.plot_comparison_dimensionless(fig=fig, color='red', marker='o
↪', markerfacecolor='None', label='H2S unary')
>>> fig, ax = ch4_unary.plot_comparison_dimensionless(fig=fig, ax=ax, color='blue',␣
↪marker='x', markerfacecolor='None', label='CH4 unary')
>>> fig, ax = h2s_binary.plot_comparison_dimensionless(fig=fig, ax=ax, color='purple',
↪ marker='d', markerfacecolor='None', label='H2S binary')
>>> fig, ax = ch4_binary.plot_comparison_dimensionless(fig=fig, ax=ax, color='cyan',␣
↪marker='s', markerfacecolor='None', label='CH4 binary')
>>> _ = ax.legend()
>>> fig.savefig('docs/source/h2s_ch4_example.png')
```

Which looks like



Having fit the isotherms, we can now evaluate them at arbitrary fugacities and temperatures. We get the same answer whether we use units or dimensional quantities

```
>>> pyo.value(h2s_unary.eval_pyomo(h2s_unary.f_ref, h2s_unary.T_ref) - h2s_unary.q_
↪ref*h2s_unary.eval_dimensionless_pyomo(1., 1.))
0.0
```

```
>>> pyo.value(
... h2s_binary.eval_pyomo(h2s_binary.f_ref, h2s_binary.f_ref, h2s_binary.T_ref)
... - h2s_binary.q_ref*h2s_binary.eval_dimensionless_pyomo(1., 1., 1.)
... )
0.0
```

3.3 Comparison to scipy

```
>>> import numpy as np
>>> popt, pcov = h2s_binary.solve_scipy()
>>> popt
array([  1.01898639, -11.07321779,  -8.15011325,  -7.32582652,
        -7.11673647])
>>> popt - np.array(list(map(pyo.value,
...          [h2s_binary.q_mi_star, h2s_binary.H_i_star, h2s_binary.H_j_star, h2s_
↪binary.A_i, h2s_binary.A_j])))
```

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```
array([-1.12501256e-06, -1.04698086e-04, -1.76342848e-04, -1.04982550e-04,
       -1.81042032e-04])
>>> h2s_binary.get_R2_scipy()
0.998828
```

which is nearly the same as the pyomo/ipopt result.

CHAPTER

FOUR

UNARY ISOTHERMS

4.1 Langmuir

The temperature-dependent unary Langmuir isotherm is expressed as

$$q_i = \frac{q_{\mathrm{m},i} k_i f_i}{1 + k_i f_i} \tag{4.1}$$

where f_i, is the fugacity of component *i*, can be calculated assuming ideal gas

$$f_i^{\mathrm{IG}} = y_i P$$

or, using the RealGas package to calculate ϕ_i from y_i, P, T data,

$$f_i = \phi_i y_i P$$

An Arrhenius relationship for k_i is assumed as

$$k_i = k_{i,\infty} \exp\left(\frac{-\Delta H_i}{RT}\right)$$

Introducing the dimensionless parameters

$$\theta_i = \frac{q_i}{q_{\mathrm{ref}}} \tag{4.2}$$

$$f_i^\star = \frac{f_i}{f_{\mathrm{ref}}} \tag{4.3}$$

$$T^\star = \frac{T}{T_{\mathrm{ref}}} \tag{4.4}$$

The variables to be fit in dimensionless form are

$$H_i^\star = \frac{\Delta H_i}{R T_{\mathrm{ref}}} \tag{4.5}$$

$$q_{\mathrm{m},i}^\star = \frac{q_{\mathrm{m},i}}{q_{\mathrm{ref}}} \tag{4.6}$$

$$A_i = \ln\left(k_{i,\infty} f_{\mathrm{ref}}\right) \tag{4.7}$$

So that Equation (4.1) becomes

$$\theta_i = \frac{q_{\mathrm{m},i}^\star \exp\left(A_i - \frac{H_i^\star}{T^\star}\right) f_i^\star}{1 + \exp\left(A_i - \frac{H_i^\star}{T^\star}\right) f_i^\star} \tag{4.8}$$

4.2 Modules

class isotherm_models.unaryisotherm.**UnaryIsotherm**(*f_i*, *q_i*, *T*, *q_ref=None*, *f_ref=None*, *T_ref=None*, ***kwargs*)

Base class for Unary Isotherms

Parameters

- **f_i** (*list*) – fugacities of component *i* (can be calculated assuming ideal gas or real gas)
- **q_i** (*list*) – loadings of component *i*
- **T** (*list, optional*) – temperatures in [K], defaults to None
- **q_ref** (*float, optional*) – reference loading, defaults to maximum loading in `q_i`
- **f_ref** (*float, optional*) – reference fugacity, defaults to maximum fugacity in `f_j`
- **T_ref** (*float, optional*) – reference temperature, defaults to maximum temperature in `T`
- **points** (*list, derived from input*) – state points at which a pressure and temperature are provided
- **f_i_star** (*list, derived*) – dimensionless fugacitities, calculated by Equation (4.3)
- **theta** (*list, derived*) – dimensionless loadings, calculated by Equation (4.2)
- **T_star** (*list, derived*) – dimensionless temperatures, calculated by Equation (4.4)
- **theta_calc** (*pyo.Var, derived from input*) – calculated dimensionless at each state point
- **objective** (*pyo.Objective, derived from input*) – objective function to be minimized for isotherm fitting, calculated from *isotherm_models.unaryisotherm.UnaryIsotherm.objective_rule_pyomo()*
- **R2** (*pyo.Expression, derived*) – coefficient of determination, see *isotherm_models.unaryisotherm.UnaryIsotherm.R2_rule()*
- **q_calc** (*pyo.Expression, derived*) – calculated loading in units

R2_rule()

Calculate coefficient of determination squared, R^2

isotherm_eq_rule(*point*)

Constraint for dimensionless expression

objective_rule_pyomo()

Sum of squared errors between calculated loading and predicted loading

$$\sum_i \left(\theta_i^{\text{raw}} - \theta_i^{\text{calc}}\right)^2$$

where *raw* denotes the raw data obtained by experiment or molecular simulation and *calc* denotes the data calculated from the isotherm function

solve(*solver=<pyomo.solvers.plugins.solvers.IPOPT.IPOPT object>*, ***kwargs*)

Solve constraints subject to objective function

Parameters

- **solver** (*pyo.SolverFactory, optional*) – solver for solving model equations, defaults to pyo.SolverFactory('ipopt')

- **kwargs** – for solve argument

class isotherm_models.unaryisotherm.**LangmuirUnary**(**args*, ***kwargs*)

Langmuir isotherm for unary mixture

Isotherm is Equation (4.1). Dimensionless isotherm is Equation (4.8). Dimensionless variables to be fit are $H_i^\star$, A_i, and $q_{\mathrm{m},i}^\star$, as defined in Equations (4.5), (4.6), and (4.7), respectively.

Parameters

- **H_i_star** (*pyo.Var*) – $H_i^\star$, dimensionless heat of adsorption of component *i*
- **A_i** (*pyo.Var*) – A_i, dimensionless langmuir constant in logarithmic space
- **q_mi_star** (*pyo.Var*) – $q_{\mathrm{m}i}^\star$, dimensionless saturation loading
- **q_mi** (*pyo.Expression*) – langmuir saturaiton loading
- **k_i_inf** (*pyo.Expression*) – langmuir adsorption constant independent of temperature
- **dH_i** (*pyo.Expression*) – heat of adsorption of component *i*

dimensionless_isotherm_expression(*point*)

Dimensionless isotherm expression, see Equation (4.8)

eval(*f_i*, *T*, *q_mi*, *k_i_inf*, *dH_i*)

evaluate using generic types (any type)

eval_pyomo(*f_i*, *T*)

evaluate using pyomo types (any type)

initial_guess_A_i()

Initial guess for A_i variable

Todo: Come up with logical initial guess

---

initial_guess_H_i_star()

Initial guess for $H_i^\star$ variable

This value of 10 corresponds to an absolute value for heat of adsorption of $10RT$ which is approximately 25 kJ/mol

initial_guess_q_mi_star()

Initial guess for $q_m i^\star$ variable

If q_{ref} is chosen to be the saturation loading, $q_m i^\star$ will be 1. Thus, we return 1 as initial guess

initial_guess_vector()

`p0` in scipy curve fit; initial guess for *dimensionless* parameters

---

Note: order here must be the same as last args in `LangmuirUnary.eval_dimensionless()`

---

isotherm_expression(*point*)

Isotherm expression in unit quantities, see Equation (4.1)

CHAPTER

FIVE

BINARY ISOTHERMS

5.1 Binary Langmuir

$$q_i = \frac{q_{\mathrm{m},i} k_i \hat{f}_i}{1 + k_i \hat{f}_i + k_j \hat{f}_j} \tag{5.1}$$

Arrhenius relationships are used for k_i and k_j, and dimensionless variables are used as illustrated in *isotherm_models.unaryisotherm.LangmuirUnary*

Note: This isotherm is not equivalent to the conventional extended langmuir isotherm, because *both* k_i and k_j are fit simultaneously to binary data.

For completeness, the relationships are repeated for the binary case below

$$k_i = k_{i,\infty} \exp\left(\frac{-\Delta H_i}{RT}\right) \tag{5.2}$$

$$k_j = k_{j,\infty} \exp\left(\frac{-\Delta H_j}{RT}\right) \tag{5.3}$$

(5.4)

The dimensionless parameters θ_i and $T^\star$ are calculated as the unary case, as shown in Equations (4.2) and (4.4), respectively. The other dimensionless parameters are

$$\hat{f}_i^\star = \frac{\hat{f}_i}{f_{\mathrm{ref}}} \tag{5.5}$$

$$\hat{f}_j^\star = \frac{\hat{f}_j}{f_{\mathrm{ref}}} \tag{5.6}$$

The dimensionless variables to be fit include $H_i^\star$, $q_{\mathrm{m},i}^\star$, A_i, $H_j^\star$, $q_{\mathrm{m},j}^\star$, and A_j. The former three ($H_i^\star$, $q_{\mathrm{m},i}^\star$, and A_i) have the same expression as the unary case, as shown in Equations (4.5), (4.6), and (4.7), respectively. The latter two are expressed as

$$H_j^\star = \frac{\Delta H_j}{R T_{\mathrm{ref}}} \tag{5.7}$$

$$A_j = \ln\left(k_{j,\infty} f_{\mathrm{ref}}\right) \tag{5.8}$$

So that Equation (5.1) becomes

$$\theta_i = \frac{q_{\mathrm{m},i}^\star \exp\left(A_i - \frac{H_i^\star}{T^\star}\right) \hat{f}_i^\star}{1 + \exp\left(A_i - \frac{H_i^\star}{T^\star}\right) \hat{f}_i^\star + \exp\left(A_j - \frac{H_j^\star}{T^\star}\right) \hat{f}_j^\star} \tag{5.9}$$

5.2 Modules

class isotherm_models.binaryisotherm.**BinaryIsotherm**(*hat_f_i*, *hat_f_j*, *q_i*, *T*, *f_ref=None*, ***kwargs*)

Base class for Binary Isotherms, inherits from UnaryIsotherm

The following additional dimensionless variables are used in computations

Parameters

- **hat_f_j** (*list*) – mixture fugacities of component *i*
- **hat_f_j** – mixture fugacities of component *j*
- **q_i** (*list*) – loadings of component *i*
- **T** (*list, optional*) – temperatures in [K], defaults to None
- **points** (*list, derived from input*) – state points at which a pressure and temperature are provided
- **hat_f_i_star** (*list, derived*) – dimensionless fugacitities of component *i*, calculated by Equation (5.5)
- **hat_f_j_star** (*list, derived*) – dimensionless fugacitities of component *j*, calculated by Equation (5.6)
- **theta** (*list, derived*) – dimensionless loadings, calculated by Equation (4.2)
- **T_star** (*list, derived*) – dimensionless temperatures, calculated by Equation (4.4)
- **theta_calc** (*pyo.Var, derived from input*) – calculated dimensionless at each state point
- **objective** (*pyo.Objective, derived from input*) – objective function to be minimized for isotherm fitting, calculated from *isotherm_models.unaryisotherm.UnaryIsotherm.objective_rule_pyomo()*
- **R2** (*pyo.Expression, derived*) – coefficient of determination, see *isotherm_models.unaryisotherm.UnaryIsotherm.R2_rule()*
- **q_calc** (*pyo.Expression, derived*) – calculated loading in units
- **unary_points** (*list, derived*) – points where only *i* is present, derived from where $\hat{f}_j < 1 \times 10^{-12}$

plot_adsorption_surface()

plot surface of adsorption data

Todo: implement this helpful for debugging

class isotherm_models.binaryisotherm.**BinaryLangmuir**(**args*, ***kwargs*)

Temperature-dependent extended unary Langmuir isotherm, expressed as

Isotherm is Equation (5.1). Dimensionless isotherm is Equation (5.9). Dimensionless variables to be fit are $H_i^\star$, A_i, $q_{\mathrm{m},i}^\star$, $H_j star$, and A_j, as defined in Equations (4.5), (4.6), (4.7), (5.7), and (5.8), respectively.

Parameters

- **H_i_star** (*pyo.Var*) – $H_i^\star$, dimensionless heat of adsorption of component *i*
- **A_i** (*pyo.Var*) – A_i, dimensionless langmuir constant in logarithmic space

- **H_j_star** (*pyo.Var*) – $H_j^\star$, dimensionless heat of adsorption of component *j*
- **A_j** (*pyo.Var*) – A_j, dimensionless langmuir constant in logarithmic space
- **q_mi_star** (*pyo.Var*) – $q_{\mathrm{m},i}^\star$, dimensionless saturation loading
- **q_mi** (*pyo.Expression*) – langmuir saturation loading
- **k_i_inf** (*pyo.Expression*) – langmuir adsorption constant independent of temperature
- **dH_i** (*pyo.Expression*) – heat of adsorption of component *i*
- **k_j_inf** (*pyo.Expression*) – langmuir adsorption constant independent of temperature
- **dH_j** (*pyo.Expression*) – heat of adsorption of component *j*

dimensionless_isotherm_expression (*point*)
Dimensionless isotherm expression, see Equation (5.9)

eval (*x*, *q_mi*, *dH_i*, *dH_j*, *k_i_inf*, *k_j_inf*)
evaluate using generic types (any type)

eval_pyomo (*hat_f_i*, *hat_f_j*, *T*)
Evaluate isotherm in dimensional form

initial_guess_vector ()
`p0` in scipy curve fit; initial guess for *dimensionless* parameters

---

Note: order here must be the same as last args in `LangmuirUnary.eval_dimensionless()`

---

isotherm_expression (*point*)
Isotherm expression in unit quantities, see Equation (5.1)

CHAPTER

SIX

ADSORPTION EQUILIBRIA RULES

For gases and their mixtures, the rules, limits, and consistency tests are [TM88]

1. Unary isotherms should reduce to Henry's law at the limit of zero pressure.
2. In spite of incorrect limits at zero pressure, both the Toth and DR equations are accurate for calculating spreading pressure provided the pressure is sufficiently high.
3. At fixed temperature and pressure, thermodynamically consistent x-y diagrams intersect each other at least once. This can be derived by considering the Gibbs adsorption isotherm at constant spreading pressure.
4. Mixed gas isotherms should display continuity with single-gas isotherms. That is,

$$\lim_{y_i \to 1} q_t = q_i \text{ (constant } P, T)$$

   where $q_t = \sum_i q_i$ is the total loading. Discontinuities generate inaccurate values of adsorbate vapor pressure that lower the quality of calculations of mixed-gas adsorption.
5. Isothermal selectivity curves for different vapor compositions should intersect at the limit of zero pressure.
6. Activity coefficients in the adsorbed phase are functions of spreading pressure as well as composition.
7. Imperfections in the gas phase led to corrections in fugacity that are small compared to the effect of nonidealities in the adsorbed phase. In most cases, vapor-phase imperfections may be ignored unless the pressure is above 500 kPa and experimental error is less than a few percent.

CHAPTER

SEVEN

REAL ADSORBED SOLUTION THEORY

Todo: implement this into the code

The *Gibbs adsorption isotherm* is

$$-a\mathrm{d}\Pi + \sum_i x_i \mathrm{d}\mu_i = 0 \tag{7.1}$$

where a is the surface area per mole of adsorbate, Π is the spreading pressure, x_i is the adsorbed mole fraction of component *i*, and μ_i is the adsorbed-phase chemical potential of component *i*.

For change in equilibrium conditions,

$$\mathrm{d}\mu_i = \mathrm{d}\mu_i^{\mathrm{g}} = RT\mathrm{d}\ln \hat{f}_i^{\mathrm{g}} \tag{7.2}$$

where $\hat{f}_i^{\mathrm{g}}$ is the fugacity of component *i* in the gas phase. And the substituting surface area of the adsorbent is

$$A = a\sum_i q_i \tag{7.3}$$

where q_i is the loading of component *i*. Substituting Equations (7.2) and (7.3) into Equation (7.1) yields

$$\frac{A}{RT}\mathrm{d}\Pi = \sum_i q_i \mathrm{d}\ln \hat{f}_i^{\mathrm{g}} \tag{7.4}$$

If we have a good description of the multicomponent isotherms,

$$q_i = F(\{\hat{f}_k\})$$

where F is an isotherm function, Equation (7.4) can be simplified to

$$\frac{A\Pi}{RT} = \sum_i \int_0^{\hat{f}_i^{\mathrm{g}}} \frac{q_i}{f_i'}\mathrm{d}f_i'$$

where f_i' is a dummy variable for integration.

CHAPTER

EIGHT

DATA SETS

8.1 CO2 and N2 on BEA

Experiment from [PXSL14]

Table 1: N2 adsorption on BEA, scanned from images in paper

P [atm]	Q [mmol/g]	T [K]	adsorbate
0.5254701189156284	0.07017543859649145	303.	N2
0.5923867910171959	0.0789473684210531	303.	N2
0.6568240613926388	0.08333333333333348	303.	N2
0.7225015761212199	0.09210526315789469	303.	N2
0.788179090849801	0.10087719298245634	303.	N2
0.8526163612252438	0.10526315789473673	303.	N2
0.9195330333268112	0.11403508771929838	303.	N2
0.9988401921780905	0.1184210526315792	303.	N2
0.41270462401356545	0.06140350877192979	303.	N2
0.47590273701602204	0.06578947368421062	303.	N2

Table 2: CO2 adsorption on BEA, scanned from images in paper

P [atm]	Q [mmol/g]	T [K]	adsorbate

continues on next page

Table 2 – continued from previous page

0.02981369160199132	0.09649122807017552	273.	CO2
0.055855562077436444	0.17543859649122817	273.	CO2
0.10917737342116132	0.3289473684210531	273.	CO2
0.24682058305615331	0.7192982456140355	273.	CO2
0.3137807343637904	0.9035087719298249	273.	CO2
0.3832192004174003	1.0877192982456143	273.	CO2
0.45017500380443043	1.254385964912281	273.	CO2
0.5171318941716123	1.4254385964912284	273.	CO2
0.5828463662253526	1.5833333333333337	273.	CO2
0.6497989086719275	1.7368421052631582	273.	CO2
0.6683960520880888	1.7763157894736845	273.	CO2
0.6894736842105261	1.8245614035087723	273.	CO2
0.7328670188482358	1.9166666666666672	273.	CO2
0.8196504271831995	2.0877192982456148	273.	CO2
0.9113904650101088	2.2587719298245617	273.	CO2
0.9994075958173001	2.4078947368421058	273.	CO2
0.15004021826561445	0.21052631578947345	303.	CO2

continues on next page

Table 2 – continued from previous page

0.21573729863692678	0.29824561403508776	303.	CO2
0.2801941346551011	0.38157894736842124	303.	CO2
0.34464988369312377	0.4605263157894739	303.	CO2
0.4103447901041326	0.5394736842105265	303.	CO2
0.4785190982412659	0.6228070175438596	303.	CO2
0.5429759342594404	0.7061403508771931	303.	CO2
0.6086686667101457	0.7763157894736845	303.	CO2
0.6731244157481683	0.8552631578947372	303.	CO2
0.7375779908258874	0.9254385964912284	303.	CO2
0.8020326528837582	1.0000000000000002	303.	CO2
0.8677253853344638	1.0701754385964914	303.	CO2
0.9321789604121826	1.1403508771929827	303.	CO2
0.9656438183438771	1.1710526315789478	303.	CO2
0.9991108502358745	1.210526315789474	303.	CO2
0.08434205091415034	0.1184210526315792	303.	CO2
0.13265397073849425	0.05701754385964941	343.	CO2
0.10539142155264239	0.052631578947368585	343.	CO2

continues on next page

Table 2 – continued from previous page

0.0595360768712363	0.02631578947368407	343.	CO2
0.20948933672471134	0.08771929824561386	343.	CO2
0.26154155525120115	0.1184210526315792	343.	CO2
0.3297017326463618	0.14473684210526327	343.	CO2
0.39414552490271526	0.17543859649122817	343.	CO2
0.4610676319050413	0.20614035087719307	343.	CO2
0.5267484075740776	0.2280701754385963	343.	CO2
0.5911911128502791	0.2543859649122808	343.	CO2
0.6581132198526054	0.2850877192982457	343.	CO2
0.7225548381486553	0.3070175438596494	343.	CO2
0.7869986304050085	0.3377192982456143	343.	CO2
0.8539196504271831	0.3640350877192984	343.	CO2
0.9196004260962194	0.38596491228070207	343.	CO2
0.9989141068284091	0.4166666666666665	343.	CO2

8.2 H2S and CH4 on MFI

Molecular simulation from [STS15],

Table 3: H2S adsorption on MFI, taken from tables in SI

P [bar]	Q [mmol/g]	d Q [mmol/g]	adsorbate	T [K]
0.001	0.01	0.0003	H2S	298
0.01	0.098	0.001	H2S	298
0.1	0.90	0.01	H2S	298
0.3	1.91	0.01	H2S	298
0.5	2.28	0.01	H2S	298
1.	2.61	0.01	H2S	298
1.5	2.742	0.004	H2S	298
2	2.810	0.005	H2S	298
3	2.90	0.01	H2S	298
4	2.95	0.01	H2S	298
5	2.983	0.004	H2S	298
6	3.010	0.003	H2S	298
7	3.030	0.004	H2S	298
8	3.050	0.004	H2S	298
9	3.064	0.004	H2S	298
10	3.079	0.003	H2S	298
0.001	0.00226	0.00002	H2S	343
0.01	0.0226	0.0002	H2S	343
0.1	0.221	0.003	H2S	343
0.3	0.62	0.01	H2S	343
0.5	0.96	0.01	H2S	343
1.	1.54	0.01	H2S	343
1.5	1.87	0.01	H2S	343
2	2.074	0.004	H2S	343
3	2.321	0.004	H2S	343
4	2.46	0.01	H2S	343
5	2.55	0.01	H2S	343
6	2.62	0.01	H2S	343
7	2.665	0.003	H2S	343
8	2.704	0.004	H2S	343
9	2.737	0.004	H2S	343
10	2.762	0.003	H2S	343
20	2.905	0.004	H2S	343
30	2.969	0.002	H2S	343
40	3.005	0.002	H2S	343
50	3.030	0.003	H2S	343

Table 4: CH4 adsorption on MFI, taken from tables in SI

P [bar]	Q [mmol/g]	d Q [mmol/g]	adsorbate	T [K]

continues on next page

Table 4 – continued from previous page

0.001	0.01	0.0003	H2S	298
0.01	0.098	0.001	H2S	298
0.1	0.90	0.01	H2S	298
0.3	1.91	0.01	H2S	298
0.5	2.28	0.01	H2S	298
1.	2.61	0.01	H2S	298
1.5	2.742	0.004	H2S	298
2	2.810	0.005	H2S	298
3	2.90	0.01	H2S	298
4	2.95	0.01	H2S	298
5	2.983	0.004	H2S	298
6	3.010	0.003	H2S	298
7	3.030	0.004	H2S	298
8	3.050	0.004	H2S	298
9	3.064	0.004	H2S	298
10	3.079	0.003	H2S	298
0.001	0.00226	0.00002	H2S	343
0.01	0.0226	0.0002	H2S	343
0.1	0.221	0.003	H2S	343
0.3	0.62	0.01	H2S	343
0.5	0.96	0.01	H2S	343
1.	1.54	0.01	H2S	343
1.5	1.87	0.01	H2S	343
2	2.074	0.004	H2S	343
3	2.321	0.004	H2S	343
4	2.46	0.01	H2S	343
5	2.55	0.01	H2S	343
6	2.62	0.01	H2S	343
7	2.665	0.003	H2S	343
8	2.704	0.004	H2S	343
9	2.737	0.004	H2S	343
10	2.762	0.003	H2S	343
20	2.905	0.004	H2S	343
30	2.969	0.002	H2S	343
40	3.005	0.002	H2S	343
50	3.030	0.003	H2S	343

Table 5: H2S/CH4 Binary adsorption on MFI, taken from tables in SI

T [K]	P [bar]	y H2S [mol/mol]	dY H2S [mol/mol]	Q H2S [mmol/g]	dQ H2S [mmol/g]	Q CH4 [mmol/g]	dQ CH4 [mmol/g]	dH H2S [kJ/mol]	d dH H2S [kJ/mol]	dH CH4 [kJ/mol]	d dH CH4 [kJ/mol]
298	1	0.00472	0.00002	0.0406	0.0001	0.499	0.001	-28.5	0.2	-19.21	0.05
298	1	0.00944	0.00004	0.0816	0.0003	0.492	0.001	-28.5	0.2	-19.22	0.02
298	1	0.0141	0.0001	0.1231	0.0005	0.483	0.001	-28.6	0.1	-19.34	0.03
298	1	0.019	0.0001	0.164	0.001	0.476	0.001	-28.6	0.1	-19.37	0.05

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Table 5 – continued from previous page

298	1	0.0239	0.0001	0.204	0.001	0.47	0.001	-28.5	0.1	-19.39	0.03
298	1	0.0288	0.0002	0.246	0.001	0.462	0.001	-28.6	0.1	-19.4	0.1
298	1	0.0337	0.0002	0.287	0.001	0.455	0.001	-28.7	0.1	-19.47	0.04
298	1	0.0385	0.0001	0.33	0.001	0.4473	0.0004	-28.7	0.1	-19.53	0.04
298	1	0.1038	0.0002	0.816	0.001	0.358	0.001	-29.4	0.1	-19.88	0.04
298	1	0.1665	0.0003	1.212	0.002	0.281	0.001	-30.07	0.03	-20.43	0.05
298	1	0.2421	0.0003	1.571	0.002	0.211	0.001	-30.82	0.05	-21	0.1
298	1	0.3341	0.0003	1.873	0.002	0.149	0.001	-31.4	0.1	-21.4	0.1
298	1	0.4433	0.0002	2.112	0.001	0.1	0.0002	-32	0.1	-21.9	0.1
298	1	0.5673	0.0001	2.295	0.001	0.0623	0.0002	-32.5	0.1	-22.2	0.2
298	1	0.7038	0.0001	2.429	0.001	0.0353	0.0002	-32.8	0.1	-22.4	0.2
298	1	0.84866	0.00002	2.534	0.001	0.0151	0.0001	-33	0.1	-22.7	0.3
298	10	0.00167	0.00002	0.0633	0.0001	1.834	0.002	-29.5	0.3	-20.19	0.03
298	10	0.00339	0.00002	0.1265	0.0001	1.796	0.002	-29.8	0.1	-20.26	0.04
298	10	0.00509	0.00001	0.1898	0.0001	1.758	0.002	-29.9	0.1	-20.35	0.03
298	10	0.0069	0.0001	0.2525	0.0003	1.717	0.002	-29.8	0.1	-20.4	0.1
298	10	0.0088	0.0001	0.315	0.0004	1.682	0.001	-30	0.1	-20.48	0.05
298	10	0.0106	0.0001	0.3784	0.0005	1.643	0.001	-30.3	0.2	-20.46	0.05
298	10	0.0128	0.0001	0.439	0.001	1.605	0.001	-29.9	0.1	-20.49	0.05
298	10	0.0147	0.0001	0.502	0.001	1.567	0.001	-30.2	0.1	-20.54	0.05
298	10	0.043	0.0002	1.235	0.001	1.11	0.001	-31.3	0.1	-21.3	0.1
298	10	0.0807	0.0001	1.789	0.001	0.758	0.001	-32.1	0.1	-21.9	0.1
298	10	0.1415	0.0003	2.251	0.001	0.465	0.001	-32.8	0.1	-22.3	0.1
298	10	0.2364	0.0003	2.575	0.001	0.265	0.001	-33.2	0.1	-22.7	0.1
298	10	0.3628	0.0002	2.773	0.001	0.15	0.001	-33	0.1	-22.4	0.1
298	10	0.5091	0.0001	2.896	0.001	0.0844	0.0004	-33.1	0.1	-22.7	0.1
298	10	0.6667	0.0001	2.977	0.001	0.0443	0.0004	-32.8	0.1	-22.2	0.2
298	10	0.83109	0.00004	3.035	0.001	0.018	0.0001	-32.9	0.1	-22.5	0.4
343	1	0.0079	0.00001	0.0169	0.0001	0.2019	0.0004	-27.8	0.2	-19.15	0.05
343	1	0.01582	0.00003	0.0338	0.0002	0.1998	0.0003	-27.9	0.1	-19.14	0.03
343	1	0.02383	0.00002	0.0504	0.0001	0.1978	0.0002	-28	0.1	-19.14	0.05
343	1	0.03177	0.00003	0.0677	0.0002	0.1955	0.0002	-28	0.1	-19.22	0.03
343	1	0.03976	0.00004	0.0849	0.0003	0.1926	0.0004	-28.1	0.1	-19.2	0.1
343	1	0.0479	0.0001	0.101	0.0004	0.1902	0.0004	-28.1	0.1	-19.2	0.1
343	1	0.0561	0.0001	0.1176	0.0004	0.1872	0.0003	-27.9	0.05	-19.2	0.1
343	1	0.064	0.0001	0.136	0.001	0.1853	0.0004	-28.1	0.1	-19.34	0.05
343	1	0.1643	0.0002	0.339	0.001	0.1577	0.0001	-28.3	0.1	-19.43	0.04
343	1	0.2519	0.0001	0.509	0.001	0.1346	0.0003	-28.47	0.04	-19.57	0.04
343	1	0.344	0.0001	0.675	0.001	0.112	0.0002	-28.75	0.05	-19.78	0.04
343	1	0.4403	0.0001	0.84	0.001	0.09	0.0002	-28.9	0.1	-19.9	0.1
343	1	0.542	0	0.995	0.001	0.0695	0.0001	-29.23	0.04	-20.11	0.03
343	1	0.6487	0.0001	1.146	0.001	0.0498	0.0001	-29.46	0.03	-20.2	0.1
343	1	0.76069	0.00004	1.285	0.001	0.0316	0.00005	-29.74	0.02	-20.6	0.1
343	1	0.87781	0.00002	1.418	0.001	0.01502	0.00005	-29.96	0.02	-20.6	0.2
343	10	0.00368	0.00002	0.0502	0.0001	1.191	0.001	-29	0.1	-19.84	0.04
343	10	0.00743	0.00004	0.1002	0.0003	1.169	0.001	-28.8	0.2	-19.85	0.02
343	10	0.01121	0.00004	0.1502	0.0003	1.146	0.001	-28.8	0.2	-19.91	0.05
343	10	0.0151	0.0001	0.2	0.001	1.124	0.002	-29	0.2	-19.92	0.04
343	10	0.0192	0.0001	0.248	0.001	1.102	0.001	-28.9	0.1	-20.01	0.03
343	10	0.0231	0.0001	0.298	0.001	1.079	0.001	-29	0.1	-20.06	0.04

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Table 5 – continued from previous page

343	10	0.027	0	0.3483	0.0002	1.056	0.002	-29	0.1	-20	0.1
343	10	0.0313	0.0001	0.396	0.001	1.036	0.002	-29.2	0.1	-20.05	0.02
343	10	0.0867	0.0005	0.97	0.003	0.78	0.001	-30	0.1	-20.8	0.1
343	10	0.1463	0.0004	1.4	0.003	0.586	0.001	-30.8	0.1	-21.2	0.1
343	10	0.2215	0.0003	1.774	0.001	0.419	0.001	-31.4	0.1	-21.8	0.1
343	10	0.3161	0.0002	2.074	0.001	0.288	0.001	-31.9	0.1	-22.09	0.05
343	10	0.4289	0.0002	2.304	0.001	0.187	0.001	-32.3	0.04	-22.5	0.1
343	10	0.5576	0.0002	2.472	0.001	0.1171	0.0004	-32.5	0.1	-22.7	0.1
343	10	0.6977	0.0001	2.595	0.001	0.0658	0.0004	-32.8	0.1	-22.7	0.2
343	10	0.84586	0.00004	2.69	0.001	0.028	0.0001	-33	0.1	-22.9	0.2
343	50	0.00243	0.00002	0.0599	0.0001	2.097	0.001	-28.5	0.1	-20.06	0.04
343	50	0.00488	0.00003	0.1198	0.0002	2.055	0.001	-28.7	0.2	-20.2	0.02
343	50	0.0075	0.0001	0.1789	0.0004	2.012	0.001	-29	0.2	-20.17	0.05
343	50	0.0101	0.0001	0.2385	0.0003	1.968	0.001	-29.1	0.2	-20.16	0.04
343	50	0.0126	0.0001	0.2979	0.0003	1.925	0.001	-28.9	0.1	-20.21	0.03
343	50	0.0154	0.0001	0.357	0.001	1.882	0.001	-29.2	0.1	-20.25	0.04
343	50	0.0183	0.0001	0.414	0.001	1.84	0.001	-29.2	0.1	-20.3	0.1
343	50	0.021	0.0002	0.474	0.001	1.798	0.001	-29.4	0.1	-20.37	0.02
343	50	0.0614	0.0004	1.152	0.002	1.306	0.002	-29.8	0.1	-20.8	0.1
343	50	0.1101	0.0002	1.657	0.001	0.941	0.001	-30.3	0.1	-21.4	0.1
343	50	0.1794	0.0002	2.081	0.001	0.637	0.001	-31	0.1	-21.8	0.1
343	50	0.2746	0.0002	2.4	0.001	0.412	0.001	-31.2	0.1	-21.96	0.05
343	50	0.3939	0.0002	2.624	0.001	0.259	0.001	-30.83	0.04	-22	0.1
343	50	0.5315	0.0003	2.776	0.002	0.157	0.001	-30.9	0.1	-22.3	0.1
343	50	0.6808	0.0001	2.885	0.001	0.0887	0.0004	-30.5	0.1	-22.1	0.2
343	50	0.8379	0.0001	2.966	0.001	0.0387	0.0002	-30.3	0.1	-23.1	0.2
298	0.001	0	0			0.0006	0.00001				
298	0.01	0	0			0.006	0.0001				
298	0.1	0	0			0.058	0.001				
298	0.3	0	0			0.168	0.003				
298	0.5	0	0			0.274	0.005				
298	1	0	0			0.5	0.01				
298	1.5	0	0			0.7	0.01				
298	2	0	0			0.85	0.01				
298	5	0	0			1.46	0.01				
298	10	0	0			1.88	0.01				
298	12	0	0			1.98	0.01				
298	15	0	0			2.09	0.01				
298	18	0	0			2.18	0.01				
298	20	0	0			2.22	0.01				
298	25	0	0			2.33	0.01				
298	30	0	0			2.39	0.01				
343	0.001	0	0			0.000217	0.000001				
343	0.01	0	0			0.00218	0.000001				
343	0.1	0	0			0.0217	0.0001				
343	0.3	0	0			0.0639	0.0003				
343	0.5	0	0			0.106	0.001				
343	1	0	0			0.204	0.001				
343	1.5	0	0			0.297	0.001				
343	2	0	0			0.379	0.001				

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Table 5 – continued from previous page

343	5	0	0			0.788	0.004				
343	10	0	0			1.213	0.003				
343	12	0	0			1.327	0.003				
343	15	0	0			1.472	0.003				
343	18	0	0			1.585	0.002				
343	20	0	0			1.643	0.003				
343	25	0	0			1.779	0.002				
343	30	0	0			1.877	0.003				
343	40	0	0			2.032	0.002				
343	50	0	0			2.141	0.002				
298	0.001	1	0	0.01	0.0003						
298	0.01	1	0	0.098	0.001						
298	0.1	1	0	0.9	0.01						
298	0.3	1	0	1.91	0.01						
298	0.5	1	0	2.28	0.01						
298	1	1	0	2.61	0.01						
298	1.5	1	0	2.742	0.004						
298	2	1	0	2.81	0.005						
298	3	1	0	2.9	0.01						
298	4	1	0	2.95	0.01						
298	5	1	0	2.983	0.004						
298	6	1	0	3.01	0.003						
298	7	1	0	3.03	0.004						
298	8	1	0	3.05	0.004						
298	9	1	0	3.064	0.004						
298	10	1	0	3.079	0.003						
343	0.001	1	0	0.00226	0.00002						
343	0.01	1	0	0.0226	0.0002						
343	0.1	1	0	0.221	0.003						
343	0.3	1	0	0.62	0.01						
343	0.5	1	0	0.96	0.01						
343	1	1	0	1.54	0.01						
343	1.5	1	0	1.87	0.01						
343	2	1	0	2.074	0.004						
343	3	1	0	2.321	0.004						
343	4	1	0	2.46	0.01						
343	5	1	0	2.55	0.01						
343	6	1	0	2.62	0.01						
343	7	1	0	2.665	0.003						
343	8	1	0	2.704	0.004						
343	9	1	0	2.737	0.004						
343	10	1	0	2.762	0.003						
343	20	1	0	2.905	0.004						
343	30	1	0	2.969	0.002						
343	40	1	0	3.005	0.002						
343	50	1	0	3.03	0.003						

8.2.1 Fugacity coefficients and fugacities

Calculated from :code`RealGas` python package using virial equation of state. The critical temperatures and densities were obtained from the TraPPE website. The accentric factors and critical compressibilities were obtained from DIPPR [RWO+07]. The critical pressure was calculated from all the other critical properties above. The k_ij parameter was set to 0.

Table 6: H2S/CH4 Binary adsorption on MFI, taken from tables in SI and added fugacities

T [K]	P [bar]	y H2S [mol/mol]	dY H2S [mol/mol]	Q H2S [mmol/g]	dQ H2S [mmol/g]	Q CH4 [mmol/g]	dQ CH4 [mmol/g]	dH H2S [kJ/mol]	d dH H2S [kJ/mol]	dH CH4 [kJ/mol]	d dH CH4 [kJ/mol]	fugacity CH4 [Pa]	fugacity H2S [Pa]	activity co-efficient CH4	activity co-efficient H2S
298	1.0	0.00472	2e-05	0.0406	0.0001	0.499	0.001	-28.5	0.2	-19.21	0.05	99354.6			0.16888041
298	1.0	0.00944	4e-05	0.0816	0.0003	0.492	0.001	-28.5	0.2	-19.22	0.02	98883.4			0.70565
298	1.0	0.0141	0.0001	0.1231	0.0005	0.483	0.001	-28.6	0.1	-19.34	0.03	98418.2			0.222372
298	1.0	0.019	0.0001	0.163				-28.6	0.1	-19.37	0.05	97929.0			0.1601208
298	1.0	0.0239	0.0001	0.204	0.001	0.47	0.001	-28.5	0.1	-19.39	0.03	97439.8			0.529528
298	1.0	0.0288	0.0002	0.246			0.001	-28.6	0.1	-19.4	0.1	96950.7			0.1966709
298	1.0	0.0337	0.0002	0.287	0.001	0.455	0.001	-28.7	0.1	-19.47	0.04	96461.5			0.2872324
298	1.0	0.0385	0.0001	0.33	0.001	0.4473	0.0004	-28.7	0.1	-19.53	0.04	95982.2			0.2718858
298	1.0	0.1038	0.0002	0.816	0.001	0.358	0.001	-29.4	0.1	-19.88	0.04	89462.2			0.2232696
298	1.0	0.1665	0.0003	1.212	0.002	0.281	0.001	-30.07	0.03	-20.43	0.05	83200.8			0.1068465
298	1.0	0.2421	0.0003	1.571	0.002	0.211		-30.82	0.05	-21.0	0.1	75650.3			0.0853799
298	1.0	0.3341	0.0003	1.873			0.001	-31.4	0.1	-21.4	0.1	66461.2			0.0606202
298	1.0	0.4433	0.0002	2.112	0.001	0.1	0.0002	-32.0	0.1	-21.9	0.1	55554.2			0.0598306
298	1.0	0.5673	0.0001	2.295	0.001	0.0623	0.0002	-32.5	0.1	-22.2	0.2	43170.6			0.0135733
298	1.0	0.7038	0.0001	2.429			0.0002	-32.8	0.1	-22.4	0.2	29543.1			0.0799454
298	1.0	0.8486	2e-05	2.534			0.0001	-33.0	0.1	-22.7	0.3	15088.8			0.0884839
298	10.0	0.00166	2e-05	0.0963	0.0001	1.834	0.002	-29.5	0.3	-20.19	0.03	98107.7			0.1531038
298	10.0	0.00339	2e-05	0.1265	0.0001	1.796	0.002	-29.8	0.1	-20.26	0.04	97938.7			0.0243572
298	10.0	0.00509	1e-05	0.1898	0.0001	1.758	0.002	-29.9	0.1	-20.35	0.03	97771.6			0.0432451

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Table 6 – continued from previous page

298	10.0	0.0069	0.0001	0.2525	0.0003	1.716	[illegible]	-29.8	0.1	-20.4	0.1	[illegible]	[illegible]	[illegible]	[illegible]
298	10.0	0.0088	0.0001	0.315	0.0004	1.682	0.001	-30.0	0.1	-20.48	0.05	[illegible]	[illegible]	[illegible]	[illegible]
298	10.0	0.0106	0.0001	0.3784	0.0005	1.643	0.001	-30.3	0.2	-20.46	0.05	[illegible]	[illegible]	[illegible]	[illegible]
298	10.0	0.0128	0.0001	0.439	0.001	1.605	0.001	-29.9	0.1	-20.49	0.05	[illegible]	[illegible]	[illegible]	[illegible]
298	10.0	0.0147	0.0001	0.502	0.001	1.567	0.001	-30.2	0.1	-20.54	0.05	[illegible]	[illegible]	[illegible]	[illegible]
298	10.0	0.043	0.0002	1.235	0.001	1.11	0.001	-31.3	0.1	-21.3	0.1	[illegible]	[illegible]	[illegible]	[illegible]
298	10.0	0.0807	0.0001	1.789	[illegible]	[illegible]	0.001	-32.1	0.1	-21.9	0.1	[illegible]	[illegible]	[illegible]	[illegible]
298	10.0	0.1415	0.0003	2.251	0.001	0.465	0.001	-32.8	0.1	-22.3	0.1	[illegible]	[illegible]	[illegible]	[illegible]
298	10.0	0.2364	0.0003	2.575	0.001	0.265	0.001	-33.2	0.1	-22.7	0.1	[illegible]	[illegible]	[illegible]	[illegible]
298	10.0	0.3628	0.0002	2.773	0.001	0.15	0.001	-33.0	0.1	-22.4	0.1	[illegible]	[illegible]	[illegible]	[illegible]
298	10.0	0.5091	0.0001	2.896	[illegible]	[illegible]	0.0004	-33.1	0.1	-22.7	0.1	[illegible]	[illegible]	[illegible]	[illegible]
298	10.0	0.6667	0.0001	2.977	0.001	0.0443	0.0004	-32.8	0.1	-22.2	0.2	[illegible]	[illegible]	[illegible]	[illegible]
298	10.0	0.8310	4e-05	3.035	0.001	0.018	[illegible]	-32.9	[illegible]	-22.5	0.4	[illegible]	[illegible]	[illegible]	[illegible]
343	1.0	0.0079	1e-05	0.0169	0.0001	0.2019	0.0004	-27.8	0.2	-19.15	0.05	[illegible]	[illegible]	[illegible]	[illegible]
343	1.0	0.0158	[illegible]	[illegible]	[illegible]	0.1998	0.0003	-27.9	0.1	-19.14	0.03	[illegible]	[illegible]	[illegible]	[illegible]
343	1.0	0.0238	2e-05	0.0504	0.0001	0.1978	0.0002	-28.0	0.1	-19.14	0.05	[illegible]	[illegible]	[illegible]	[illegible]
343	1.0	0.0317	[illegible]	[illegible]	[illegible]	0.1955	0.0002	-28.0	0.1	-19.22	0.03	[illegible]	[illegible]	[illegible]	[illegible]
343	1.0	0.0397	[illegible]	[illegible]	[illegible]	0.1926	0.0004	-28.1	0.1	-19.2	0.1	[illegible]	[illegible]	[illegible]	[illegible]
343	1.0	0.0479	0.0001	[illegible]	[illegible]	[illegible]	0.0004	-28.1	0.1	-19.2	0.1	[illegible]	[illegible]	[illegible]	[illegible]
343	1.0	0.0561	0.0001	0.1176	0.0004	0.1872	0.0003	-27.9	0.05	-19.2	0.1	[illegible]	[illegible]	[illegible]	[illegible]
343	1.0	0.064	0.0001	0.136	0.001	0.1853	0.0004	-28.1	0.1	-19.34	0.05	[illegible]	[illegible]	[illegible]	[illegible]
343	1.0	0.1643	0.0002	[illegible]	[illegible]	[illegible]	0.0001	-28.3	0.1	-19.43	0.04	[illegible]	[illegible]	[illegible]	[illegible]
343	1.0	0.2519	0.0001	0.509	0.001	0.1346	0.0003	-28.47	0.04	-19.57	0.04	[illegible]	[illegible]	[illegible]	[illegible]
343	1.0	0.344	0.0001	0.675	0.001	[illegible]	[illegible]	-28.75	0.05	-19.78	0.04	[illegible]	[illegible]	[illegible]	[illegible]
343	1.0	0.4403	0.0001	0.84	0.001	0.09	0.0002	-28.9	0.1	-19.9	0.1	[illegible]	[illegible]	[illegible]	[illegible]

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Table 6 – continued from previous page

343	1.0	0.542	0.0	0.995	0.001	0.0695	0.0001	-29.23	0.04	-20.11	0.03	45739.5
343	1.0	0.6487	0.0001	1.146	0.001	0.0498	0.0001	-29.46	0.03	-20.2	0.1	35078.5
343	1.0	0.76069	4e-05	1.285	0.001	0.0316	5e-05	-29.74	0.02	-20.6	0.1	23891.7
343	1.0	0.8778	2e-05	1.408	0.001	0.0151	5e-05	-29.96	0.02	-20.6	0.2	12196.3
343	10.0	0.00367	2e-05	0.0502	0.0001	1.191	0.001	-29.0	0.1	-19.84	0.04	98641.2
343	10.0	0.00743	4e-05	0.1002	0.0003	1.169	0.001	-28.8	0.2	-19.85	0.02	98269.8
343	10.0	0.01124	4e-05	0.1502	0.0003	1.146	0.001	-28.8	0.2	-19.91	0.05	97895.5
343	10.0	0.0151	0.0001	0.2	0.001	1.124	0.002	-29.0	0.2	-19.92	0.04	97510.3
343	10.0	0.0192	0.0001	0.248	0.001	1.102	0.001	-28.9	0.1	-20.01	0.03	97104.2
343	10.0	0.0231	0.0001	0.298	0.001	1.079	0.001	-29.0	0.1	-20.06	0.04	96717.9
343	10.0	0.0270	0.0001	0.348	0.0003	1.056	0.002	-29.0	0.1	-20.0	0.1	96331
343	10.0	0.0313	0.0001	0.396	0.001	1.036	0.002	-29.2	0.1	-20.05	0.02	95905
343	10.0	0.0867	0.0005	0.97	0.003	0.78	0.001	-30.0	0.1	-20.8	0.1	90414
343	10.0	0.1463	0.0004	1.4	0.003	0.586	0.001	-30.8	0.1	-21.2	0.1	84500
343	10.0	0.2215	0.0003	1.774	0.001	0.419	0.001	-31.4	0.1	-21.8	0.1	77033
343	10.0	0.3161	0.0002	2.074	0.001	0.288	0.0000	-31.9	0.1	-22.09	0.05	67634
343	10.0	0.4289	0.0002	2.304	0.0001	0.187	0.001	-32.3	0.04	-22.5	0.1	56426
343	10.0	0.5576	0.0002	2.472	0.001	0.1171	0.0004	-32.5	0.1	-22.7	0.1	43649
343	10.0	0.6977	0.0001	2.595	0.001	0.0658	0.0004	-32.8	0.1	-22.7	0.2	29768
343	10.0	0.8458	6e-05	2.69	0.001	0.0279	0.0001	-33.0	0.1	-22.9	0.2	15140
343	50.0	0.00243	2e-05	0.0599	0.0001	2.097	0.001	-28.5	0.1	-20.06	0.04	47447
343	50.0	0.00488	2e-05	0.1199	0.0001	2.055	0.001	-28.7	0.2	-20.2	0.02	47330
343	50.0	0.0075	0.0001	0.1789	0.0004	2.012	0.001	-29.0	0.2	-20.17	0.05	47205
343	50.0	0.0101	0.0001	0.2385	0.0003	1.968	0.0000	-29.1	20.2	-20.16	0.04	47082
343	50.0	0.0126	0.0001	0.2979	0.0003	1.925	0.001	-28.9	0.1	-20.21	0.03	46963

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Table 6 – continued from previous page

343	50.0	0.0154	0.0001	0.357	0.001	1.882	0.001	-29.2	0.1	-20.25	0.04	46829	3317072
343	50.0	0.0183	0.0001	0.414	0.001	1.84	0.001	-29.2	0.1	-20.3	0.1	46691	9599435
343	50.0	0.021	0.0002	0.474	0.001	1.798	0.001	-29.4	0.1	-20.37	0.02	46562	7987947
343	50.0	0.0614	0.0004	1.152	0.002	1.306	0.002	-29.8	0.1	-20.8	0.1	44633	4009018
343	50.0	0.1101	0.0002	1.656	0.001	0.998	0.001	-30.3	0.1	-21.4	0.1	42297	313028
343	50.0	0.1794	0.0002	2.081	0.001	0.637	0.001	-31.0	0.1	-21.8	0.1	38960	115033
343	50.0	0.2746	0.0002	2.4	0.001	0.412	0.0001	-31.2	0.1	-21.96	0.05	34358	0969102
343	50.0	0.3939	0.0002	2.623	0.001	0.259	0.001	-30.83	0.04	-22.0	0.1	28580	2380158
343	50.0	0.5315	0.0003	2.776	0.002	0.167	0.001	-30.9	0.1	-22.3	0.1	21936	779559
343	50.0	0.6808	0.0001	2.885	0.001	0.0887	0.0004	-30.5	0.1	-22.1	0.2	14796	528205
343	50.0	0.8379	0.0001	2.966	0.001	0.0387	0.0002	-30.3	0.1	-23.1	0.2	7415	2669677
298	0.001	0.0	0.0			0.0006	1e-05					99.9998	25678685702
298	0.01	0.0	0.0			0.006	0.0001					999.98	8256782245007
298	0.1	0.0	0.0			0.057	0.001					9998.2	25691898507
298	0.3	0.0	0.0			0.168	0.003					29984.	771668401699
298	0.5	0.0	0.0			0.273	0.005					49956.	128763272727252
298	1.0	0.0	0.0			0.5	0.01					99825.	258559885853
298	1.5	0.0	0.0			0.7	0.01					14960	8856631716 51
298	2.0	0.0	0.0			0.85	0.01					19930	519604768256
298	5.0	0.0	0.0			1.46	0.01					49566	321710848644
298	10.0	0.0	0.0			1.88	0.01					98271	7187344915213
298	12.0	0.0	0.0			1.98	0.01					11751	298484848924458
298	15.0	0.0	0.0			2.09	0.01					14612	290417 2045708
298	18.0	0.0	0.0			2.18	0.01					17443	1089934418183
298	20.0	0.0	0.0			2.22	0.01					19314	736111120617
298	25.0	0.0	0.0			2.33	0.01					23933	2551739490429
298	30.0	0.0	0.0			2.39	0.01					28471	046968973215 7
343	0.001	0.0	0.0			0.0002	1e-06					99.9999	0005807724
343	0.01	0.0	0.0			0.0021	8e-06					999.990	0058526717
343	0.1	0.0	0.0			0.0217	0.0001					9999.0	0063021331 6
343	0.3	0.0	0.0			0.0639	0.0003					29991.	700219025 1959
343	0.5	0.0	0.0			0.106	0.001					49975.	004149706745
343	1.0	0.0	0.0			0.204	0.001					99900.	0010795265506
343	1.5	0.0	0.0			0.297	0.001					14977	019935429392
343	2.0	0.0	0.0			0.379	0.001					19960	031568952136
343	5.0	0.0	0.0			0.787	0.001					49750	015366091204 2
343	10.0	0.0	0.0			1.213	0.003					99005	055787576132

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343	12.0	0.0	0.0			1.327	0.003					1185694.0117021980785931018158			
343	15.0	0.0	0.0			1.472	0.003					1477680.07120228154205141481456			
343	18.0	0.0	0.0			1.585	0.002					1767908.0237989802271290999 2235			
343	20.0	0.0	0.0			1.643	0.003					1960420.0980589145210049029 0725			
343	25.0	0.0	0.0			1.7790000020000001						2438310.0151952374562406078 09398			
343	30.0	0.0	0.0			1.876999999999998						2911387.0821865204362427395 5068			
343	40.0	0.0	0.0			2.032	0.002					3843246.9608703608117402175 766			
343	50.0	0.0	0.0			2.141	0.002					4756285.0117691951125702353 82224			
298	0.001	1.0	0.0	0.01	0.0003							0.0	99.9992561196499699925611964946		
298	0.01	1.0	0.0	0.098	0.001							0.0	999.9256144550079799256144550077		
298	0.1	1.0	0.0	0.9	0.01							0.0	9992.5639349519112563934951112		
298	0.3	1.0	0.0	1.91	0.01							0.0	29933.1251670891745708389260582		
298	0.5	1.0	0.0	2.28	0.01							0.0	49814.3746435829462874928716486		
298	1.0	1.0	0.0	2.61	0.01							0.0	99258.8768452479555887684524755		
298	1.5	1.0	0.0	2.742	0.004							0.0	148335.5663361918894037755740742		
298	2.0	1.0	0.0	2.81	0.005							0.0	197046.4926510985232463258002		
298	3.0	1.0	0.0	2.9	0.01							0.0	293379.2032033977930677344 6589		
298	4.0	1.0	0.0	2.95	0.01							0.0	388273.2026629972068300665 74301		
298	5.0	1.0	0.0	2.983	0.004							0.0	481744.5250679262458905013 58445		
298	6.0	1.0	0.0	3.01	0.003							0.0	573809.0458150756348409691 7834		
298	7.0	1.0	0.0	3.03	0.004							0.0	664482.4831302145926069018 74506		
298	8.0	1.0	0.0	3.05	0.004							0.0	753780.3995308946225499413 5085		
298	9.0	1.0	0.0	3.063999999999996								0.0	841718.2032606935724244806 7373		
298	10.0	1.0	0.0	3.078999999999997								0.0	928311.1497310972831114973 1672		
343	0.001	1.0	0.0	0.0022600000000000003 05								0.0	99.9995185661669999518566 16649		
343	0.01	1.0	0.0	0.0226	0.0002							0.0	999.9518576596399951857659 6396		
343	0.1	1.0	0.0	0.221	0.003							0.0	9995.1868087882995186808788291		
343	0.3	1.0	0.0	0.62	0.01							0.0	29956.7021258789186567375292702		
343	0.5	1.0	0.0	0.96	0.01							0.0	49879.7859980159745957199603149		
343	1.0	1.0	0.0	1.54	0.01							0.0	99519.7220483139521972204831392		
343	1.5	1.0	0.0	1.87	0.01							0.0	148920.6731505597284487670 3815		
343	2.0	1.0	0.0	2.074	0.004							0.0	198083.5015314979241750765 73659		
343	3.0	1.0	0.0	2.320999999999997								0.0	295698.2252215985660750738 4488		
343	4.0	1.0	0.0	2.46	0.01							0.0	392370.7357896980926839474 2285		
343	5.0	1.0	0.0	2.55	0.01							0.0	488107.8320710974215664142 0627		
343	6.0	1.0	0.0	2.62	0.01							0.0	582916.2693276955271155462 826		
343	7.0	1.0	0.0	2.665	0.003							0.0	676802.7595109636861085015 662		
343	8.0	1.0	0.0	2.703999999999997								0.0	769773.9715207962217464400 899		
343	9.0	1.0	0.0	2.737	0.004							0.0	861836.5314648957859614607 21086		
343	10.0	1.0	0.0	2.762	0.003							0.0	952997.0229163928299702291 63286		
343	20.0	1.0	0.0	2.905	0.004							0.0	1816406.651370470820332568 73854		
343	30.0	1.0	0.0	2.969	0.002							0.0	2596545.196748865515065582 787		
343	40.0	1.0	0.0	3.005	0.002							0.0	3299333.123158502483328078 96269		
343	50.0	1.0	0.0	3.03	0.003							0.0	3930318.304974786063660994 8226		

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