**8.15** The molar integral heat of solution $\Delta_s \underline{H}$ is defined as the change in enthalpy that results when 1 mole of solute (component 1) is isothermally mixed with $N_2$ moles of solvent (component 2) and is given by

$$\Delta_s \underline{H} = (1 + N_2)\underline{H}_{mix} - \underline{H}_1 - N_2 \underline{H}_2$$
$$= \overline{H}_1 + N_2 \overline{H}_2 - \underline{H}_1 - N_2 \underline{H}_2$$

$\Delta_s \underline{H}$ is easily measured in an isothermal calorimeter by monitoring the heat evolved or absorbed on successive additions of solvent to a given amount of solute. The table below gives the integral heat-of-solution data for 1 mol of sulfuric acid in water at 25°C (the negative sign indicates that heat is evolved in the dilution process).

| | | | | |
|---|---|---|---|---|
| $N_2$ (moles of water) | 0.25 | 1.0 | 1.5 | 2.33 |
| $-\Delta_s \underline{H}$ (J) | 8242 | 28 200 | 34 980 | 44 690 |
| $N_2$ (moles of water) | 4.0 | 5.44 | 9.0 | |
| $-\Delta_s \underline{H}$ (J) | 54 440 | 58 370 | 62 800 | |
| $N_2$ (moles of water) | 10.1 | 19.0 | 20.0 | |
| $-\Delta_s \underline{H}$ (J) | 64 850 | 70 710 | 71 970 | |

**a.** Calculate the heat evolved when 100 g of pure sulfuric acid is added isothermally to 100 g of water.

$$100\text{g } H_2SO_4 \times \frac{1 \text{ mol } H_2SO_4}{98.079 \text{ g}} = 1.020 \text{ mol } H_2SO_4$$

$$100 \text{ g } H_2O \times \frac{1 \text{ mol } H_2O}{18.02 \text{ g}} = 5.55 \text{ mol } H_2SO_4$$

now we want to get this onto a basis of how many moles $N_2$ per 1 mol $N_1$

$$\frac{5.55 \text{ mol}}{1.020 \text{ mol}} = 5.44 \frac{\text{mol water}}{\text{mol acid}}$$

luckily 5.44 is directly in the given data

$$-58370 \frac{J}{\text{mol acid}} \times 1.02 \text{ mol acid} = \boxed{-59513 \text{ J}}$$

water.

**b.** Calculate the heat evolved when the solution prepared in part (a) is diluted with an additional 100 g of water.

now $\quad 200\,g \text{ water} \times \frac{1\,mol}{18.02} = 11.10\ mol\ H_2O$

$$\frac{11.10\ mol\ H_2O}{1.020\ mol\ H_2SO_4} = 10.88$$

interpolating yields $\quad \Delta_s \underline{H} = 65376\ J/mol\ acid$

$$\Delta_s H = -65376 \times 1.02\ J$$

Q1 Answer

but heat already released so

$$\Delta_s H = -65376 \times 1.02 + 59513 = \boxed{-7136\ J}$$

**c.** Calculate the heat evolved when 100 g of a 60 wt % solution of sulfuric acid is mixed with 75 g of a 25 wt % sulfuric acid solution.

100 g of 60 wt% $= 0.61\ mol\ H_2SO_4$ ; $2.22\ mol\ H_2O$

$= 3.63\ \frac{mol\ H_2O}{mol\ H_2SO_4}$ (ratio 1)

75 g of 25 % $= 0.19\ mol\ H_2SO_4$, $3.12\ mol\ H_2O$

$= 16.33\ \frac{mol\ H_2O}{mol\ H_2SO_4}$ (ratio 2)

final $\quad 6.80\ mol\ H_2SO_4$, $5.34\ mol\ H_2O$

$= 6.65\ \frac{mol\ H_2O}{mol\ H_2SO_4}$ (ratio 3)

the $\Delta_s \underline{H}$ may now be interpolated to get

```python
N2 = np.array([0.25, 1.0, 1.5, 2.33, 4.0, 5.44, 9.0, 10.1, 19.0, 20.0])
delH = np.array([8242, 28200, 34980, 44690, 54440, 58370, 62800, 64850, 70710, 71970])

# ratios are the mole ratios for each of the solutions (both added and the final)
result1, result2, result3 = np.interp(ratio1, N2, delH), np.interp(ratio2, N2, delH), np.interp(ratio3, N2, delH)
print(f'first interpolated: {result1:.0f} \nsecond interpolated: {result2:.0f} \nfinal interpolated: {result3:.0f}')
```

✓ 0.0s

```
first interpolated: 52277
second interpolated: 68954
final interpolated: 59881
```

$\frac{J}{1 \text{ mol acid}}$

now to find the total heat evolved we find the total evolved of the final and subtract the heat from the original solutions

$$\Delta_s H = n_{H_2SO_4} \Delta_s \underline{H}_{final} - \sum_{i=1}^{2} n_{H_2SO_4, i} \Delta_s \underline{H}_i$$

$$= 0.803(-59881) - \left[0.612(-52277) + 0.191(-68954)\right]$$

$$\boxed{= -2917 \text{ J}}$$

**d.** Relate $(\overline{H}_1 - \underline{H}_1)$ and $(\overline{H}_2 - \underline{H}_2)$ to only $N_1$, $N_2$, $\Delta\underline{H}_s$, and the derivatives of $\Delta\underline{H}_s$ with respect to the ratio $N_2/N_1$.

$$\Delta_s \underline{H} = (\overline{H}_1 - \underline{H}_1) + \frac{N_2}{N_1}(\overline{H}_2 - \underline{H}_2)$$

now taking the partial and doing the product rule correctly

$$\frac{\partial(\Delta_s \underline{H})}{\partial(N_2/N_1)} = \frac{\partial}{\partial(N_2/N_1)}\left[\overline{H}_1 - \underline{H}_1\right] + (\overline{H}_2 - \underline{H}_2) + \frac{N_2}{N_1}\frac{\partial}{\partial(N_2/N_1)}\left[\overline{H}_2 - \underline{H}_2\right]$$

multiply both sides by $N_1$ now to turn like terms into a sum

$$N_1 \frac{\partial \Delta_s \underline{H}}{\partial(N_2/N_1)} = N_1(\overline{H}_2 - \underline{H}_2) + \sum_{i=1}^{2} N_i \frac{\partial}{\partial N_2/N_1}\left[\overline{H}_i - \underline{H}_i\right]$$

This solution is actually my magnum opus.

The partial of a constant is zero, so get rid of $\underline{H}_i$

$$\frac{\partial \Delta_s \underline{H}}{\partial (N_2/N_1)} = (\bar{H}_2 - \underline{H}_2) + \sum_{i=1} N_i \frac{\partial \bar{H}_i}{\partial (N_2/N_1)}$$

and now it is clear the last term is 0 by Gibbs-Duhem

$$\frac{\partial \Delta_s \underline{H}}{\partial (N_2/N_1)} = \bar{H}_2 - \underline{H}_2$$

now since $\bar{H}_2 - \underline{H}_2$ is known

$$\Delta_s \underline{H} = (\bar{H}_1 - \underline{H}_1) + \frac{N_2}{N_1}(\bar{H}_2 - \underline{H}_2)$$

$$\bar{H}_1 - \underline{H}_1 = \Delta_s \underline{H} - \frac{N_2}{N_1}(\bar{H}_2 - \underline{H}_2)$$

$$\bar{H}_1 - \underline{H}_1 = \Delta_s \underline{H} - \frac{N_2}{N_1}\left[\frac{\partial \Delta_s \underline{H}}{\partial (N_2/N_1)}\right]$$

**e.** Compute the numerical values of $(\bar{H}_1 - \underline{H}_1)$ and $(\bar{H}_2 - \underline{H}_2)$ in a 50 wt % sulfuric acid solution.

assume 100g basis for easy calculations

50 g $H_2O$, 50g $H_2SO_4$ $\Longrightarrow$ 0.510 mol $H_2SO_4$, 2.78 mol $H_2O$

$$\frac{N_2}{N_1} = 5.444 \ \frac{\text{mol } H_2O}{\text{mol } H_2SO_4}$$

See next page for code using equations derived earlier !!

# cheg325 homework1 q4 coding

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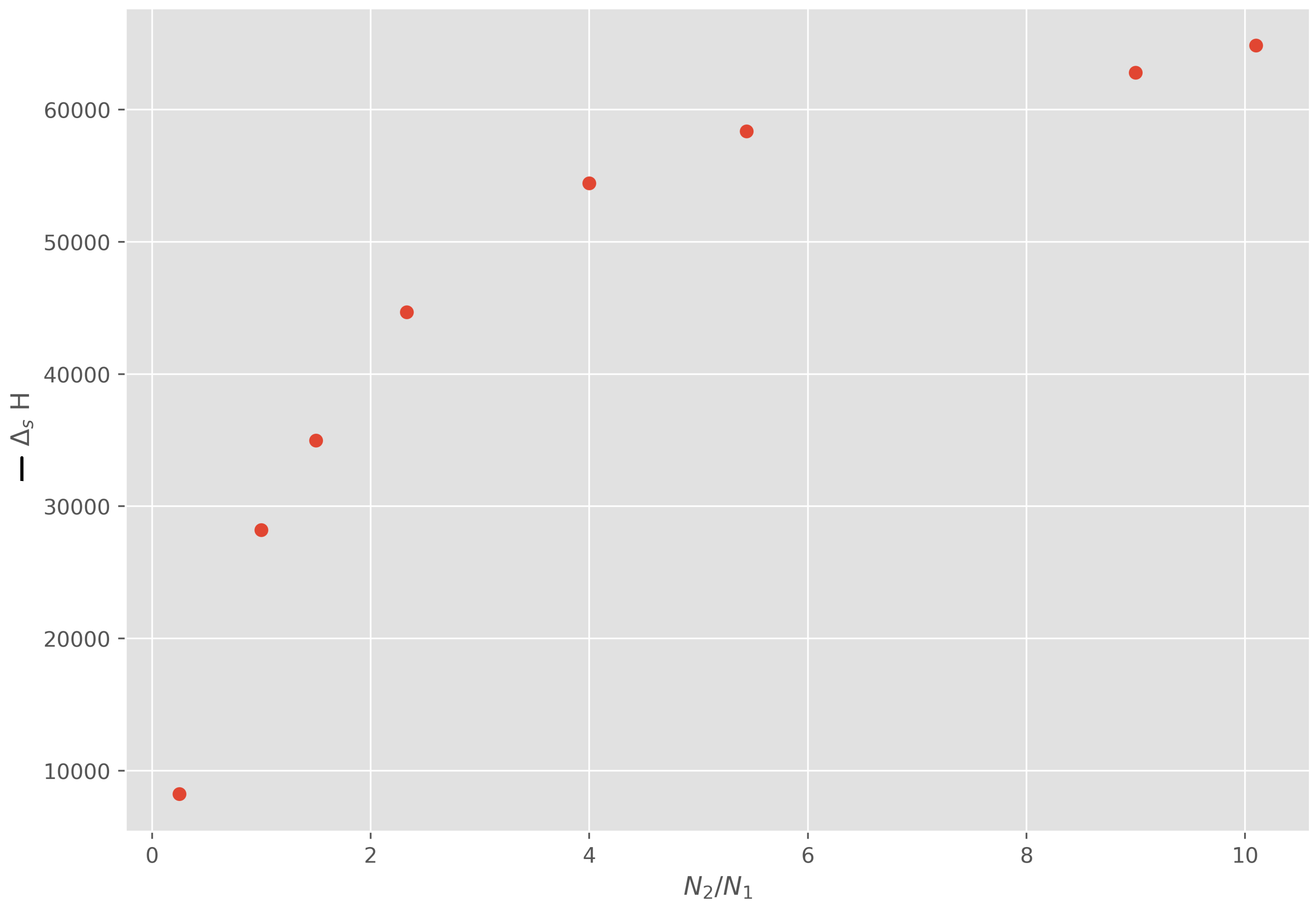
```python
import numpy as np
import matplotlib.pyplot as plt
from scipy.optimize import curve_fit
plt.style.use('ggplot')
```

I'll bring the data in as arrays and plot it to get a feel for how it looks. I also removed the 2 greatest points since they're quite far from the others

```python
N2 = np.array([0.25, 1.0, 1.5, 2.33, 4.0, 5.44, 9.0, 10.1, ])
delH = np.array([8242, 28200, 34980, 44690, 54440, 58370, 62800, 64850, ])
fig, ax = plt.subplots(figsize=(10,7), dpi=500, subplot_kw={'xlabel':'$N_2 / N_1$', 'ylab
ax.scatter(N2, delH);
```




after some trial and error, it looks like the equation fits well to this form of equation

$$y = a + b \cdot \exp\left(c \cdot x^d\right)$$

where $a, b, c, d$ are fit parameters and also

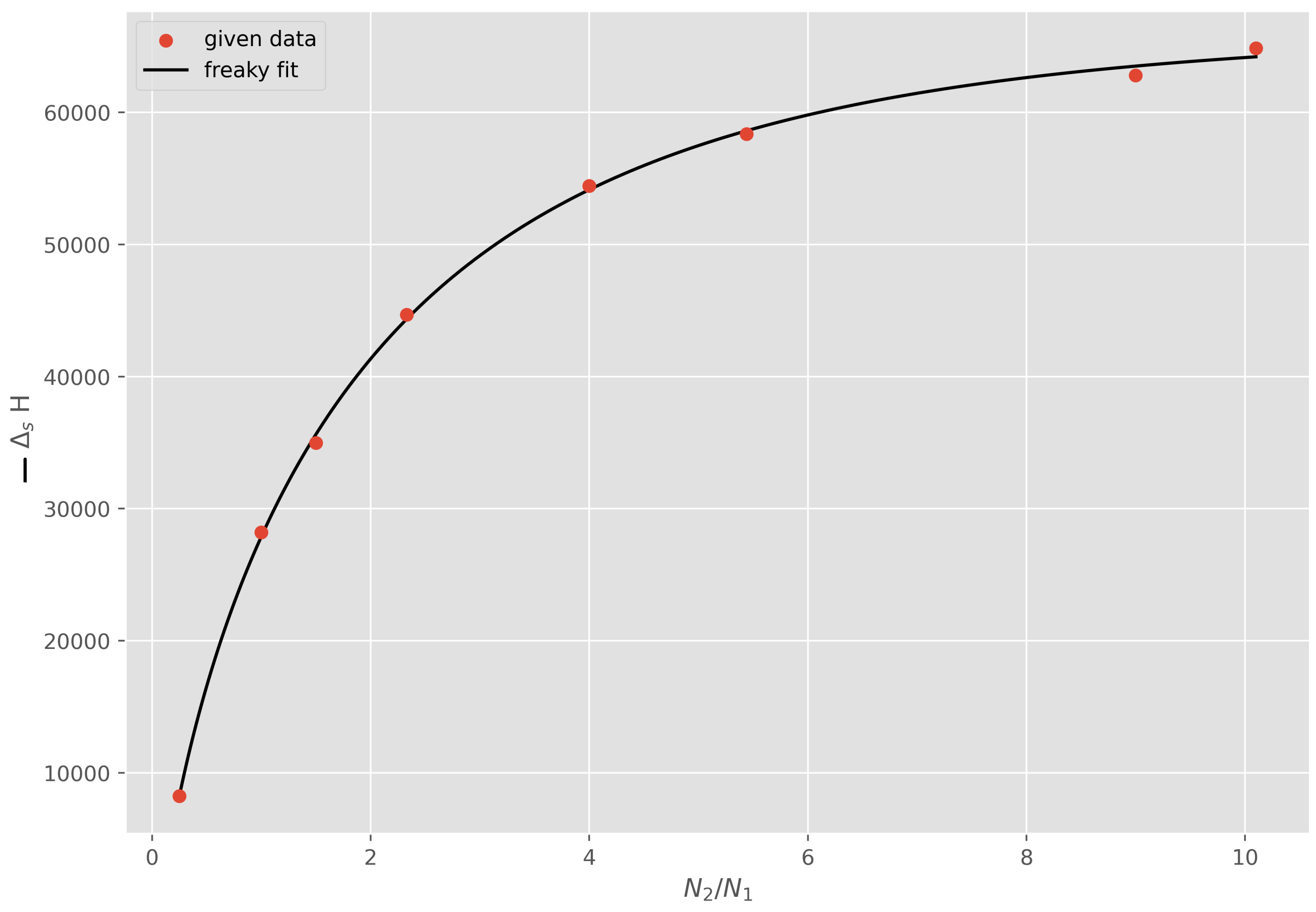
$$y' = b \cdot c \cdot d \cdot x^{d-1} \cdot \exp\left(c \cdot x^d\right)$$

```python
def func(n2, a, b, c, d):
    return a + b * np.exp(c * n2 ** d)

def derivative_func(n2, a, b, c, d):
    return b * c * d * (n2 ** (d-1)) * np.exp(c * n2 ** d)

popt = curve_fit(func, N2, delH, p0=[90000,0,-1, 1])
a, b, c, d = popt[0]

fig, ax = plt.subplots(figsize=(10,7), dpi=500, subplot_kw={'xlabel':'$N_2 / N_1$', 'ylab
ax.scatter(N2, delH, zorder=10)
x = np.linspace(N2.min(), N2.max(),1000)
ax.plot(x, func(x, a, b, c, d), c='black')
ax.legend(['given data', 'freaky fit']);
```




now that we have a fit and the derivative of the fit, we may evaluate the derivative at 50% and finish up this question.

first, i'll calculate the moles of each and the $N_2/N_1$

```python
N_acid = 50 / 98.079
N_water = 50 / 18.015
ratio = N_water / N_acid
print(f'mol acid: {N_acid:.4f},\nmol water: {N_water:.4f},\nratio: {ratio:.4f}')
```

```
mol acid: 0.5098,
mol water: 2.7755,
ratio: 5.4443
```

also, remember that the data was given as $-\Delta_s \underline{H}$ and this negative must be accounted for in my final answer

```python
h2_h2 = derivative_func(ratio, a, b, c, d)
print(f'(H2 - H2) = {-h2_h2:.1f}')
h1_h1 = func(ratio, a, b, c, d) - (N_water / N_acid) * h2_h2
print(f'(H1 - H1) = {-h1_h1:.1f}')
```

```
(H2 - H2) = -2347.3
(H1 - H1) = -45834.6
```

so our final result is

$$(\bar{H}_2 - \underline{H}_2) = -2347.3 \ \frac{\mathrm{J}}{\mathrm{mol}}$$

$$(\bar{H}_1 - \underline{H}_1) = -45834.6 \ \frac{\mathrm{J}}{\mathrm{mol}}$$