ChE 212: Phase Equilibrium and Chemical Separations

Hydrogen Sulfide (H₂S) Separation

Parts a and b are modified from Wankat 12.D2. with additional context on H_2S .

You are creating a process to remove hydrogen sulfide (H_2S) from a feed gas. H_2S is a gas commonly found during the drilling and production of crude oil and natural gas, as well as in wastewater treatment and utility facilities and sewers [1].

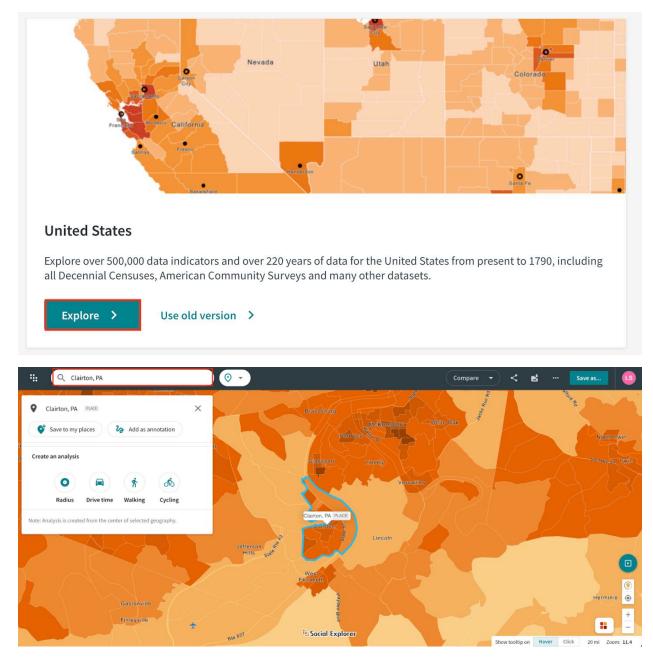
Not only is H_2S considered a pollutant, lowering the value of the product stream, but is hazardous to human health; it is classified by OSHA as both "an irritant and chemical asphyxiant with effects on both oxygen utilization and the central nervous system" [1]. Dosages above 100 ppm can kill a person within a few breaths [1]. For these reasons, the Bureau of Labor Statistics (BLS) cites it as the leading cause of workplace gas inhalation deaths in the United States [2].

To safely remove the H_2S , you will absorb it into water at 15 degrees C. The water entering for absorption is pure (e.g. mole fraction $H_2O = 1$) and is at a flow rate of 2,000 kmol/hr. The feed gas being cleaned initially contains 0.12 mol% H_2S and has a flow rate of 10.0 kmol/hr. You can assume both the gas and liquid flow rates remain constant throughout absorption. The total pressure is 2.5 atm. Your goal is to recover 97% of the H_2S in the water.

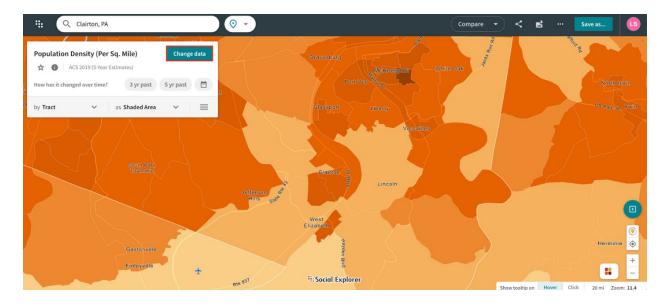
- a. Calculate the outlet gas and liquid mole fractions of H_2S .
- b. Calculate the number of equilibrium stages needed using a McCabe Thiele Diagram.

Parts c, d, and e will require you to research using outside sources and explore demographic data on <u>Social Explorer</u>. You can access content on Social Explorer by creating a free (e.g. Northwestern-sponsored account) using your Northwestern email.

- c. Based on the mole fraction of H₂S now in the feed gas, if this stream leaked into the environment, would you be in violation of the Clean Air Act? What limits, if any, exist for H₂S release into ambient air? <u>This review paper</u>, specifically "H₂S Regulation in the US" may be helpful [3].
- d. Read about what has been happening regarding hydrogen sulfide exposure in Mon Valley, PA. Briefly describe (one paragraph of 3-5 sentences) what you learned. Consider including:
 - i. What is happening with hydrogen sulfide there?
 - ii. Where is the H_2S coming from?
 - iii. What steps have been taken so far in response?
- e. Now that you know the context for Mon Valley, let's look more specifically at the demographics of the area. To do this, we will use an interactive mapping software linked to census data called <u>Social Explorer</u>. Once logged in to your free account, click "Explore" under the United States map. In the search bar at the top, type in "Clairton, PA" to put you inside the Mon Valley area.



Rather than look at population density (the default), we want to change the data to look at <u>race</u> and <u>income</u>. Note that there are dozens of other datasets, and by no means are race and income comprehensive demographics of an area with complex communities and identities present. For the sake of our analysis, these areas will provide additional insight.



Change data	Q X
Categories All data (by source) Saved	
2012 2013 2014 2015 2016 20	2017 2018 2019 2020 2021 2022 ;
	Show all years
	0
Population	Age
Sex Sex	Race
Sex Sex	касе
S Income	Family Structure
Marital Status	Group Quarters
Unmarried Partners	Education
Housing	House Value
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Explore Mon Valley using the Race and Income data for 2019. Compare the racial and economic status of Clairton, PA (Allegheny County, Census Tract 4927, 4928, 4929) where the US Steel Mill is versus West Mifflin, PA (Allegheny County, Census Tract 3102, 4883, 4885) upwind. What may this indicate about the relationship between chemical plants, pollution, and marginalized communities more broadly?

f. What process may you recommend to a company that is producing H₂S that is over the threshold, rather than emitting or burning it? (<u>Hint</u>: What process produces the most elemental sulfur?)

Solutions

Parts a & b. Part a and the first graph are from Wankat. The second graph is one I created for the assignment, with a table of values I used. They come from the same information in Part a.

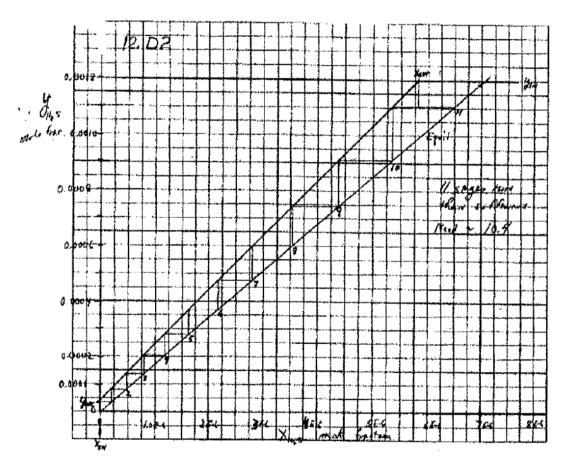
12,D2.

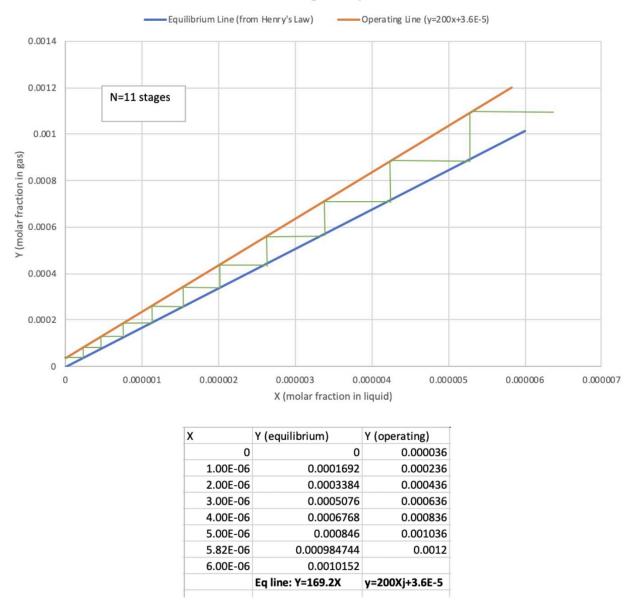
a) L & V constant, 97% rec. H₂S –
$$\therefore$$
 3% left in gas.
y_{eut} = 0.03 0.0012 = 0.000036

Equil.: $y = \frac{p_{H_2S}}{p_{tot}} = \frac{423x}{2.5} = 169.2x$ M.B. with Const. L & V: 0.0012 V = 0.000036 V + $x_{out}L$

$$x_{out} = 0.0012 - 0.000036 \frac{V}{L} = 0.001164 \frac{10}{2000} = 5.82E - 6$$

b) See Figure. $y = \frac{L}{V} \mathbf{x} + \frac{L}{V} \mathbf{y}_{in} - \mathbf{x}_{out}$ where $\mathbf{y}_{in}, \mathbf{x}_{out}$ & $\mathbf{y}_{out}, \mathbf{x}_{in}$ are on op, line.





12.2D Stage Analysis

Grading for Parts c, d, and e should be based on effort shown, thoughtfulness, and completion of the prompt. Example answers are given here to show what answers could look like and key points to bring up in discussion with students after completion.

Part c.

Despite being in the U.S. EPA's list of Extremely Hazardous Substances as determined by the Emergency Planning and Community Right-To-Know Act in the event of accidental releases, there are no limits under

the Clean Air Act for H_2S in ambient air [4]. As a result, many states have chosen to set their own limits, per recommendations by agencies like Agency for Toxic Substances and Disease Registry (ATSDR), National Institute for Occupational Safety and Health (NIOSH), and the American Conference of Governmental Industrial Hygienists (ACGIH) typically around 0.005 ppm [4]. Thus, at 0.000036 M or 0.036 ppm, the gas stream is in excess of many state limits but technically is not regulated in this manner by the EPA.

It is worth noting H_2S is regulated by OSHA in a workplace setting in industries where H_2S is found over the threshold quantity of 1,500 pounds (680.38 kg) [4]. Some movement has been made toward regulations, but it has generally been slow. The last advance was, starting in 2011, U.S. companies were required to report their emissions of H_2S to the Toxic Release Inventory (TRI), a system for tracking toxic chemicals that may pose environmental and health risks [4].

Part d.

As H_2S is not regulated under the Clean Air Act, the state of Pennsylvania has its own 24-hour H_2S concentration maximum set at 0.005 ppm [4]. As of April 21, 2021, in 2021 alone, U.S. Steel in Mon Valley, PA, has exceeded this limit 13 times, as seen in the figure below [4]. The Allegheny County Health Department (ACHD) submitted a Notice of Violation (NOV), covering incidents both in 2021 (13) and in 2020 (25) and with civil penalties up to \$25,000 for continued violation [4]. U.S. Steel has 14 days to meet with ACHD to work toward a resolution before they will proceed with legal action [4]. Over the last two years, a number of civilians have mobilized, through protests and the formation of the Group Against Smog and Pollution (GASP), to put pressure for stricter enforcement and spread awareness of the dangers of high exposures.

H ₂ S concentrations at ACHD air quality monitors 1/1/2021 - 4/18/2021 on days with at least one exceedance of the state 24-hour average standard (ppm)					
date	Liberty		North Braddock		
date	1-hour max	24-hour average	1-hour max	24-hour average	
2/21/2021	0.021	0.004	0.071	0.010	
3/3/2021	0.020	0.006	0.077	0.011	
3/8/2021	0.020	0.006	0.023	0.004	
3/9/2021	0.019	0.008	0.045	0.012	
3/10/2021	0.032	0.008	0.021	0.004	
3/11/2021	0.030	0.009	0.027	0.006	
3/25/2021	0.031	0.008	0.081	0.010	
3/27/2021	0.027	0.008	0.033	0.010	
4/3/2021	0.013	0.006	0.026	0.006	
4/5/2021	0.032	0.006	0.026	0.006	
4/6/2021	0.034	0.007	0.003	0.001	
4/7/2021	0.040	0.009	0.007	0.002	
4/13/2021	0.018	0.006	0.026	0.005	
4/18/2021	0.028	0.006	0.025	0.004	

Part e.

Clairton, PA (Allegheny County, Census Tract 4927, 4928, 4929) where the US Steel Mill has a much higher proportion of BIPOC (Black, Indigenous, People of Color) residents and a bit higher population of Latinx residents than West Mifflin, PA (Allegheny County, Census Tract 3102, 4883, 4885) has. In fact, the discrepancy is as large as 40% of the population in that census tract of a difference, despite the relative proximity. Furthermore, the Clairton census tracts displayed high percentages of below-poverty line incomes (< 25,000 for a family of four in Pennsylvania [5]) by ~10% more of the population than the West Mifflin tracts.

It is not a coincidence that race and income stratification exists in Mon Valley. The problem is dual-sided. Local and federal policy, like redlining (refuse a loan or insurance to someone because they live in an area deemed to be a poor financial risk, historically African American communities) and zoning (the allocation of land to be used for specific purposes) in the United States has led to large plots of cheap land more often available near marginalized and/or lower-income communities.

Yet this problem also exists because many chemical plants have also failed to properly assess the environmental and human/societal impact of their plant/process. Because the population demographics near chemical plants are disproportionately higher in minoritized groups, those groups have increased exposure to harmful chemicals and increased negative health outcomes.

Without effective local or federal regulation/punishment, as has been long delayed in Mon Valley, manufacturers are emboldened to pollute more. This vicious cycle only further compounds the harm the chemical industry causes underserved communities.

Part f.

Most elemental sulfur is produced via the Claus Process, which converts H_2S and O_2 into water and elemental sulfur (see reaction schema below) [6]. H_2S conversion is typically around 75% through one catalytic reactor and can be as high as 98% with an additional one or two stages [6]. Not only do you convert a toxic pollutant to inert compounds, but that elemental sulfur can be sold for additional profit.

$$H_2S + 1 \frac{1}{2} O_2 \rightarrow SO_2 + H_2O$$

 $2 H_2S + SO_2 \rightarrow 2 H_2O + 3 S^1$

 $3 H_2S + 1 \frac{1}{2} O_2 \rightarrow 3 H_2O + 3 S$

References

- 1. *Hydrogen Sulfide Overview. Occupational Safety and Health Administration* (OSHA). (n.d.). <u>https://www.osha.gov/hydrogen-sulfide</u>.
- U.S. Bureau of Labor Statistics. (2020, December 22). Census of Fatal Occupational Injuries (CFOI) - Current and Revised Data. U.S. Bureau of Labor Statistics. https://www.bls.gov/iif/oshcfoi1.htm.
- Malone Rubright, S. L., Pearce, L. L., & Peterson, J. (2017). Environmental Toxicology of Hydrogen Sulfide. *Nitric Oxide: Biology and Chemistry*, 71, 1–13. <u>https://doi.org/10.1016/j.niox.2017.09.011</u>.
- Group Against Smog and Pollution. (2021, April 21). Another Weekend, Another H2S Air Quality Exceedance for Mon Valley. pgh.org. <u>https://gasp-pgh.org/2021/04/19/another-weekend-anotherh2s-air-quality-exceedance-for-monvalley/?utm_source=rss&utm_medium=rss&utm_campaign=another-weekend-anotherh2s-air-quality-exceedance-for-mon-valley.
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- Pennsylvania Income Eligibility. PA Department of Community & Economic Development. (2021, February 23). <u>https://dced.pa.gov/housing-and-development/weatherization/incomeeligibility/</u>.
- 6. Department of Energy (DOE). (n.d.). *The Claus Process*. netl.doe.gov. https://netl.doe.gov/research/coal/energy-systems/gasification/gasifipedia/claus-process.