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An Introduction to Adsorption

1. Overview

Recently, after I finished a talk on the thermodynamics of adsorption, an audience member stood up with a critical comment. "But adsorption has been studied for over a hundred years." Yes, exactly!

Serious studies of adsorption have been ongoing for over a hundred years now. Qualitative knowledge of adsorption goes back thousands of years. This is not to the detriment of the field. Rather it is a testament to the broad utility of adsorption and the complexity of trying to understand such a diverse array of phenomena.

Adsorption is the densification of a fluid at an interface. The nature of the interface may be solid-liquid, gas-liquid, liquid-liquid or solid-gas. In this work we focus on adsorption between a solid "adsorbent" and a gaseous "adsorptive species" which is denoted the "adsorbate" in the adsorbed phase. Adsorption is strictly an interfacial phenomenon, unlike "absorption" wherein the absorptive species penetrates the absorbent. Each molecule in the adsorbed phase actually has less entropy than in the bulk gas phase; however it also has a reduced enthalpy owing to attractive interactions at the interface. This sets up the basic equilibrium of adsorption: a reduction in entropy compared to the gas phase is balanced by a comparable reduction in enthalpy. Adsorption is thus an exothermic process. The favorable interactions at the interface, which enable all adsorption, may be of chemical or physical nature. When chemical bonds occur between the adsorbent and the adsorbate the phenomenon is called chemisorption. When only physical interactions are present (e.g. van der

Waals forces), it is called physisorption. "Sorption" is a more general term used for the ambiguous case. In general, chemisorption results in much stronger adsorbent-adsorbate interactions and is effective at higher temperatures, but requires specific adsorbate-adsorbent systems and is less reversible. In this work we focus on physisorptive systems.

2. Pores

The uses of physisorption are extremely diverse, the most primary of which is the characterization of the adsorbents themselves. Solid-gas physisorption may occur on any solid, but as an interfacial phenomenon, physisorption is strictly a surface effect. High surface area materials, especially porous materials, therefore lend themselves to adsorptive studies. Often porous materials can only be easily and effectively characterized by physisorption. The pores of a porous material may be broadly lumped into one of three size categories: macropores, mesopores and micropores. Macropores are greater than 50 nanometers in width. Mesopores have widths between 2 and 50 nanometers. Micropores have widths of less than 2 nanometers. Both micropores and mesopores are considered "nanopores". Pores are typically modeled as either cylinders with unique pore diameters, or slits with unique pore widths. Macropores, mesopores and micropores each physisorb gases in distinct ways and require different modeling.

In macropores the pore walls are sufficiently well separated to have non-overlapping effects. This is because physical interactions like van der Waals forces fall off rapidly with distance. Macropores can thus be treated in the same way as a nonporous material, where only a single surface is considered at a time. In macropores, layer-by-layer adsorption is expected and can be effectively modeled using Brunauer, Emmett and Teller (BET) Theory. BET Theory has proven highly successful in determining the surface area of macroporous

adsorbents. Using subcritical adsorption isotherm measurements of nitrogen, argon, carbon dioxide or krypton (for low surface area adsorbents), up to near-saturation pressures, the monolayer coverage can be solved from BET Theory. This quantitative monolayer coverage is in turn correlated with a specific surface area based on the size of the adsorbate molecule. One caveat is that different results may be obtained with different gases (probe molecules) as different pores and topologies are accessible to different size probe molecules.

Mesopores may be treated in much the same way as macropores, with the additional complication of capillary condensation. In appropriately sized mesopores, surface tension (through capillary action) can cause the adsorptive species to condense into a liquid phase in the mesopores at pressures below the bulk saturation pressure. This phenomenon is unique to mesopores as macropores are too large and micropores are too small. Capillary condensation results in hysteresis between the adsorption and desorption isotherms. However, the presence of capillary condensation can be used to obtain information about the pore-size distribution via the Kelvin Equation and variants.

Micropores are of similar dimensions to the gases adsorbed. Within micropores, opposite pore walls often exhibit overlapping potentials. Thus micropores are more accurately treated with a pore-filling model than a layer-by-layer model for adsorption. In general the adsorptive species will holistically fill the micropore volume, making metrics of specific micropore volume more important than specific surface area. The micropore volume may be determined empirically with the Dubinin-Radushkevich equation and variants. Moreover, of critical importance, the micropore-size distribution may be obtained semi-empirically via nonlocal density functional theory (NLDFT). As such, physisorption may be used to characterize pores varying in size from 0.35 nanometers to greater than 100 nanometers.

3. Applications

Adsorbents are also widely used in industrial scale processes like catalysis and gas separation. Catalysis is an enabling factor in ~90% of chemical and materials manufacturing worldwide and may employ homogeneous or heterogeneous catalysts.[1] Unlike homogeneous catalysts, heterogeneous catalysts are of a different phase than the underlying reaction. Often porous solids are used as heterogeneous catalysts in conjunction with a liquid or gas phase. The fluid phase is first adsorbed onto the catalyst, followed by dissociation of the fluid, surface diffusion, a surface reaction and finally desorption of the product. Adsorption is thus a prerequisite for most heterogeneous catalysis and a fundamental understanding of the adsorption process is vital. Moreover, as adsorbents typically have large accessible surface areas, they may be used as structural supports that keep catalysts well dispersed to maximize efficacy.

Gas separation and purification is a second key industrial use of adsorption. Separating chemically inert gases or otherwise removing gaseous impurities is often done by cryogenic distillation. For gases with similar boiling points this process can be both expensive and energy intensive. Gas separation using physisorption offers an efficient alternative, especially when high levels of purity are not required. In physisorptive separation, gases are flowed through an adsorbent bed where one gas preferentially adsorbs over another, ideally with great selectivity. The adsorbent bed may then be regenerated by reducing the pressure or increasing the temperature to desorb the adsorbate. These cyclic processes are referred to as Pressure Swing Adsorption (PSA) and Temperature Swing Adsorption (TSA), respectively. The selectivity is typically due to differences in the adsorbent-adsorbate physical interactions between each gas and the adsorbent. In some cases steric effects are used to enhance selectivity when the gases

to be separated are of dissimilar size or shape and only small and correctly shaped molecules can penetrate a well-defined pore structure. This is commonly used to dry steam from the cracking process or to dry natural gas using zeolites with well-defined micropore structures. Kinetic separation mechanisms may also be employed in molecular sieves where non-uniform pore size distributions allow different molecules to diffuse at different rates. One common example is the separation of nitrogen from air using molecular sieves. Overall, adsorption offers an efficient means of gas separation, purification and in some cases solvent recovery from both industrial and vented sources.

4. Krypton

In this work we study krypton adsorption in detail as a step towards improving krypton separation from other inert gases. Krypton, the fourth noble gas, is an unreactive monatomic gas that otherwise bears many similarities to methane. The two gases share a similar size (Kr: 3.9 Å, CH_4: 4.0 Å)[2] and approximately spherical symmetry, as well as similar boiling points (120 K and 112 K, respectively)[3] and critical temperatures (209 K and 190 K, respectively). Conveniently, monatomic krypton allows for very simple calculations of thermodynamic properties such as entropy, since rotational and internal vibrational modes do not exist. Krypton has applications in the photography, lighting[4] and medical industries[5,6], and is commonly used as an adsorbate for characterizing low-surface-area materials[7,8]. There is also significant active interest in finding a cost effective and efficient means of separating krypton from xenon derived from nuclear waste[9,10].

Nuclear power plants supply over 10% of the world's electricity and are a valuable source of energy in the United States.[11] Unfortunately, the United States is already fraught with over 70,000 tons of nuclear waste and no good storage options[12,13]. One avenue towards

diminishing the amount of nuclear waste generated in the future is to reprocess spent nuclear fuel. Reprocessing entails chopping up and dissolving spent nuclear fuel to recover fissionable remains. These remains can be used to generate additional electricity often exceeding 25% of the initial generation.[14] While the US does not currently reprocess nuclear fuel, reprocessing is typical in Europe, Russia and Japan, and as a member of the International Framework for Nuclear Energy Cooperation, the US has partnered with other countries to improve and develop closed nuclear fuel cycles with reprocessing. During reprocessing, radioactive krypton-85 and nonradioactive xenon are off-gassed. As a radioactive mixture, these gases should be stored as radioactive waste, often in inefficient mole fraction of ~90% nonradioactive xenon to ~10% radioactive krypton-85.[15] While cryogenic distillation is an energy intensive means of separating krypton from xenon, adsorbents offer a potentially efficient alternative. With properly tuned adsorptive separation, less nonradioactive xenon would need to be stored, putting less stress on current nuclear waste storage options.

5. Natural Gas

Another large and quickly growing application of physisorption is for the densified storage of natural gas, particularly within the transportation sector. This is a major focus of this thesis.

Natural gas powers 22% of the world and 33% of the US, and yet its importance is projected to grow.[16] From 2010 to 2013 worldwide natural gas consumption has grown at a rate of 2% annually from 113,858 to 121,357 billion cubic feet.[16] Over the same time, the proven reserves have grown at a rate of 1% annually, up to 6,972.518 trillion cubic feet.[16]

Assuming a 2% annual increase in consumption, but no increase in the proven reserves, our current proven reserves will last into the 23rd century, although estimates vary.[16]

Natural gas predominantly originates from two naturally occurring processes. Biogenic methane results when methanogenic archaea break organic matter into simple hydrocarbons like methane. These microorganism live in oxygen depleted regions of the earth's crust and in the intestines of most animals. Collecting the gases emanating from manure and landfills has proven a clean and renewable source of natural gas. Nonetheless, to date these operations are small scale and pale in comparison to the scope of thermogenic natural gas collection. Thermogenic methane is synthesized from ancient organic matter under the high temperatures and pressures found deep in the earth's crust. This process takes millions of years and is thus not considered renewable on a human timescale. These natural gas fossil fuels are often discovered alongside oil, although deeper deposits synthesized at higher temperatures tip the balance towards a higher fraction of natural gas synthesis.

Thermogenic methane is also found alongside coal (coalbed gas) or as a methane hydrate (clathrate). Methane hydrates form under temperatures below 15 °C and pressures greater than 19 bar. These conditions are met in offshore continental shelves and the permafrost of Siberia. Recently Japan Oil, Gas and Metals National Cooperation has recovered commercially viable quantities of natural gas from oceanic methane clathrates.[17] This presents a particularly exciting advancement given estimates of vast quantities of oceanic methane hydrates (estimated at 5×10^{15} cubic meters of methane hydrate).[16]

Other unconventional sources of natural gas have been studied and commercialized within the past decade. These sources have historically been economically prohibitive, but this is changing with recent technological advancements. The collection of deep gas, tight gas, and

shale gas are on the rise. Shale gas, in particular has boomed from less than 1% of the US

natural gas production in 2000 to 39% in 2012.[16] It is estimated that there may be more than a

quadrillion cubic feet of unconventional natural gas reserves in the US alone.[16]

At present, 15 countries account for 84% of worldwide natural gas production, with

Russia, Iran, Qatar, Turkmenistan and the US at the top of the list.[16] Before transportation or

use, the natural gas must be purified. Impurities like water, sand and other gases are separated

out. Some of the purified gas byproducts like propane, butane and hydrogen sulfide are sold

on secondary markets. Landfill methane is prone to have large quantities of carbon dioxide

and hydrogen sulfide, which must be removed before transportation to prevent pipeline

corrosion. The gas may be further purified to achieve a high quality gas comprised of almost

pure methane and known as "dry" natural gas. In the presence of significant quantities of

other hydrocarbons, natural gas is deemed "wet". The main constituent in natural gas is always

methane, followed by ethane. The composition varies significantly but is generally in

accordance with Table 1.

Table 1. Typical Composition of Natural Gas[18]

gas	mole fraction (%)
methane	87-97
ethane	1.5-7
propane	0.1-1.5
butane	0.02-0.6
alkanes #C > 4	trace
nitrogen	0.2-5.5
carbon dioxide	0.1-1.0
oxygen	0.01-0.1
hydrogen	trace

The transportation and utilization of natural gas has been employed since 500 B.C. when Chinese in the Ziliujing district of Sichuan developed crude natural gas pipelines from bamboo.[19] This natural gas was harnessed to boil seawater. It wasn't until 1785, however, that natural gas first found widespread commercialization as a fuel for streetlamps and homes in England.[19] This natural gas emanated from fissures above naturally occurring pockets. In 1821 William A. Hart drilled the first intentional natural gas well, in Fredonia, New York.[19] Since then the industry has exploded in the US and abroad. An emerging natural gas industry set to explode is for use in the transportation sector. Worldwide tens of millions of natural gas vehicles dot the roads. Ordinary internal combustions engines can be converted to run on natural gas for less than $10,000 and commercial vehicles designed specifically to run on natural gas are gaining traction. Starting in 2008 with the Honda Civic natural gas, major auto manufacturers have churned out a number of compressed natural gas commercial vehicles including the Chevrolet Silverado 2500, Dodge Ram 2500, Ford F-250 and Chevrolet Savana.

This surge in natural gas cars proffers environmental benefits. For the same amount of energy, thermogenic methane emits 16% less carbon dioxide than diesel.[16] Landfill biogas can emit a net 88% less carbon dioxide than diesel.[16] In power generation, methane power plants emit almost 50% less carbon dioxide than coal-powered plants.[16] The carbon dioxide released per million BTU, for a variety of common fuels, is listed in Table 2. Methane is the cleanest burning hydrocarbon. Additionally, natural gas emits less trace pollutants including carbon monoxide, nitrogen oxides, sulfur oxides and particular matter than other fuels.

Table 2. Pounds of CO_2 Emissions Per MBTU for Common Fuels[16]

fuel	Lbs. CO_2/MBTU
Coal (anthracite)	228.6
Coal (bituminous)	205.7
Coal (lignite)	215.4
Coal (subbituminous)	214.3
Diesel fuel & heating oil	161.3
Gasoline	157.2
Propane	139
Natural Gas	117

The main hindrance to wide implementation of natural gas in the transportation sector stems from the onboard storage problem. Natural gas has a high gravimetric energy density of 56 MJ kg^{-1}, competitive with other fuel sources, but an abysmally low volumetric energy density of 37 MJ m^{-3} at standard conditions.[3] This is a common problem for gaseous fuels with critical temperatures significantly below room temperature. Three potential solutions have been separately implemented in commercial applications: cryogenic liquefaction, high-pressure compression, and compression in the presence of adsorbent materials.

Cryogenic liquefaction requires cooling natural gas to below the critical temperature of methane, which is 190K. This is typically achieved with liquid nitrogen as a coolant in a cryogenic setup. While cryogenic liquefaction can achieve volumetric energy densities as high as 22 GJ m^{-3}, it is an energy intensive process and requires expensive equipment and monitoring[3]. These drawbacks have thus far prevented the widespread adoption of cryogenic liquefaction as a means for natural gas storage on privately owned vehicles.

At high pressures of 700 bar, natural gas has a volumetric energy density of ~17 GJ m^{-3}.[3] However, high-pressure compression requires specialized storage tanks. As pressure requirements are increased, the requisite class of storage tank shifts from Type I (all metal, which is the cheapest and currently makes up 93% of the onboard natural gas storage market) to Type IV, all composite with high associated costs.[20] Moreover, high pressures limit potential tank designs (as a necessity of eliminating weak points) and potentially pose a significant threat if ruptured intentionally or unintentionally.

The use of adsorbents and moderate compression allows for significant volumetric energy density improvements over pure compression at moderate pressures and temperatures. At low and moderate pressures the favorable interactions between the adsorbent and the adsorbate densify natural gas under equilibrium conditions. Improved natural gas storage is a significant subject of inquiry in this thesis.

Adsorption also serves a number of other niche purposes in areas such as heat pumps and spacecraft environmental controls.[21] All told, adsorption spans chemistry, biology, physics and engineering and is an integral part of our world. It demands further fundamental scientific inquiry and expertise in adsorbent engineering.

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