

Physical Sorption of Gases: Implications for Resources, Reserves, and Production from Sorbed Gas Reservoir Systems

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Despite its importance in the production of natural gas from sorbed gas reservoir systems, the mechanism of physical sorption is frequently inaccurately described, modeled, and measured. A better understanding and description of sorption will lead to improved modeling of reservoir behavior and better estimation of gas resources and reserves. The present overview seeks to correct some common misunderstandings regarding the nature of sorption, clarify some of the terminology used to describe it, identify some significant sources of uncertainty in measurement, and describe the behavior of sorbed gases during production.

Sorbed gas reservoirs are multi-component, multi-phase geologic systems wherein a significant fraction of the gas resource occurs in a condensed state *in situ* (under initial reservoir conditions), but transforms to a gaseous state as pressure is reduced during production. This phase transition is fundamentally identical to the release of solution gas from the liquid phase in “black oil” reservoirs. If a distinct gas phase is not initially present, a gas phase will form (i.e. the system will “boil”) at a fluid pressure equal to the sum of the vapor pressures of all the volatile components in the system, described as the *critical desorption pressure*, or as *bubble point pressure*.

The term *sorption* broadly describes a system where a condensed phase(s)—termed the *sorbent*—incorporates a volatile substance—termed the *sorbate*—into its structure, by physical bonding. Classically, the sorbent is a solid, and the sorbate is a gas, but more broadly, either the sorbent or sorbate can be a liquid, depending on system composition, pressure, and temperature. To a degree, compositional distinction between the sorbent and sorbate is made relative a particular set of reference conditions—typically at laboratory conditions (~1 atm and ~25°C). Important sorbates in sorbed gas reservoir systems are CH₄, CO₂, N₂, C₂₊ hydrocarbons, and H₂O. Methane is usually the most important sorbate from a resource perspective.

The most important sorbent for methane is sedimentary organic matter (OM), which is comprised of a complex, heterogeneous mixture of widely varying composition that may be solid, liquid, or a mixture of both. The inorganic (mineral) fraction of the reservoir may also act as a sorbent, but its contribution to sorption capacity is (apparently) small, difficult to measure, and dependent on mineralogy. Depending on its type and maturity, sedimentary OM is comprised of an infinite variety of organic constituents, spanning a vast range of molecular weights, from methane at the low end to complex three dimensional macromolecules at the other. The term OM is often understood to refer solely to the residual material that remains in laboratory specimens after volatile components have escaped, but this distinction is subjective. The larger macromolecules may include cross linkages, which provide a semi-rigid three-dimensional structure of low molecular density. Vacant regions (porosity) within this structure extend down to nanometer scale or less, potentially providing accessibility to small sorbate molecules such as water and methane.

A significant proportion of the *free volume* in sorbed gas reservoirs is associated with the OM, even in shales where the OM content may be just a few volume-%. The term *porosity* is ambiguous when describing this system, as the accessible volume varies for different species and measurement

procedures. Porosity, such as it exists, not only presents a molecular surface for sorption, but, if of sufficient dimensions, may be occupied by a distinct fluid phase (either liquid or gas). The behavior of water is complex, in that it may function both as a sorbate (when dispersed within the solid phase(s)), or as a weak sorbent when present as a distinct liquid phase. Both as a sorbate and pore-filling fluid, water reduces accessibility to methane.

Sorbed molecules retain the same chemical composition, but none of the characteristics, of a gas. As such, sorption can be regarded as a phase transformation, where either the sorbed molecules or the sorbent-sorbate interface may be treated thermodynamically as a distinct phase. Transition from the gas phase to sorbed phase entails a loss of kinetic, vibrational, and rotational energy with attendant release of heat, roughly proportional to the strength of the sorption bond. Heats of sorption are reported to be in the range of 3 to 5 kcal/mole, based on measurements made on coal. Comparable values have not yet been reported for shales. Thermodynamic equilibrium is established between the sorbed phase(s) and the gas phase when their chemical potential(s), or Gibbs free energies, are equal. Notably, dissolved methane in an aqueous phase (if present) will be in equilibrium with methane in any other condensed phases present, as well as with the gas phase (if present).

The terms *absorption* and *adsorption* are ambiguous. *Absorption* broadly describes the uptake of one substance within another. In contrast, *adsorption* describes a situation where molecules of the sorbate are concentrated on discrete molecular surfaces that have a more-or-less fixed (i.e. solid) topology and surface energy. The term *solvation* describes the uptake of a gas by a liquid or solid, or uptake of liquid by a solid, where evidence of solvation is expressed as volumetric swelling of the sorbent owing to bond interactions with the sorbate. The term *sorption* encompasses both adsorption and solvation, and as such, correctly describes the behavior of heterogeneous, multi-phase sorbents that lack a rigid, well-defined physical structure, such as OM. A further ambiguity of the term *adsorption* is that it may describe either a state of (dynamic) equilibrium involving physical bonding on a surface *or* a dynamic mass transfer process entailing net flux of sorbate into the sorbent.

The term *desorption* (s.l.) describes an associated set of dynamic processes resulting in a net flux of sorbate molecules out of the sorbent. Desorption will occur when changes in state variables result in the sorbed phase being out of equilibrium with surrounding phases, as, for example, when system pressure is decreased, or temperature is increased. Physical bonds related to sorption are of very short duration, lasting just 10^{-6} to 10^{-9} seconds. Thus, desorption entails repeated adsorption/desorption steps, accompanied simultaneously by some mechanism of mass transport through the interconnected pore network. For this reason, sorption is effectively a statistical phenomenon, where at any given moment, the vast majority of sorbed molecules occur in the bonded state, whereas in the gas phase—essentially by definition—the vast majority occur in the non-bonded state.

Empirical measurements in the laboratory can be used to establish the equilibrium relationship between the sorbate in the gas phase and the condensed (sorbed) phase. Sorbate pressure serves as a surrogate measure of chemical potential in the gas phase. Sorbate concentrations within the sorbent may be measured either volumetrically or gravimetrically at constant temperature over a range of pressures, with the resultant equilibrium relationship being termed a *sorption isotherm*. The term *adsorption isotherm* is ambiguous; and there is no value or necessity for the term *desorption isotherm*. Although the sorption isotherm is usually described as representing the equilibrium sorption capacity of the sorbent as a function of sorbate pressure, it also represents the equilibrium vapor pressure curve of a particular sorbent-sorbate system as a function of sorbate concentration.

Accurate measurements of the concentration of sorbed species are handicapped by an imprecise understanding of the physical properties of the sorbate within the sorbent. Of particular concern is that the molar volume of the sorbed phase is generally unknown, and must be approximated. This problem is all the more difficult when condensation to liquid phase occurs within the microporosity, as for H₂O and CO₂. Moreover, as the sorbent (OM) is heterogeneous, this parameter is likely to represent a range of values, rather than a single value.

Chemists have struggled for decades to develop a mathematical model that accurately describes the sorption behavior of coal and other forms of OM. No single model has proven to be universally applicable across all conditions of temperature and pressure. The most widely used is the Langmuir model, which offers the advantage of being both mathematically simple and reasonably accurate. The Langmuir model assumes, however, that the accessible molecular surface area is fixed and invariant, that all sorption sites are chemically equivalent (energetically homogeneous), and that there is no interaction between sorbate molecules (i.e. all sorbate molecules behave identically). None of these assumptions is correct in detail, yet the Langmuir model works reasonably well in most cases.

The shape of the Langmuir isotherm is defined by the Langmuir Volume, V_L , which is the theoretical maximum sorption capacity, approached asymptotically at infinite pressure, and the Langmuir Pressure, P_L ; which mathematically represents the pressure at which the Langmuir Volume is 50% filled. These parameters, however, are principally employed for empirical curve-fitting, and have limited physical significance. The Langmuir isotherm is also characterized by its initial slope at negligible concentrations (or at low pressures), which is termed the Henry's Law coefficient, which partially provides an indication of the accessible surface area, as well as the strength of the sorption bond.

V_L and P_L both vary as a function of sorbent composition, especially as related to OM rank and type. Solvation of a sorbate within a liquid phase produces an isotherm having a considerably different shape, displaying a much more linear relationship between sorbate partial pressure and concentration. At low concentrations, this linear relationship is termed Henry's Law. Sorption isotherms for heterogeneous sorbed gas reservoir systems appear to represent a hybrid form that includes contributions of Henry's Law solvation, and Langmuir-type (ad)sorption. The presence of organic liquids in the system might conceivably either enhance or suppress methane sorption capacity. If the liquid occurs as a distinct phase and if methane solubility is high, total sorption capacity can be high and roughly linear with pressure, as evidenced in some shales. If, however, the liquid is dispersed through a microporous (semi)solid matrix, methane sorption may be suppressed due to the phenomenon of pore-plugging, as evidenced in some coals of bituminous rank.

A diagram similar in appearance to the methane sorption isotherm can be used to depict the *total* methane capacity of the reservoir system as a function of *total* system pressure. On this diagram, the actual isotherm curve (s.s.) represents a phase boundary separating a two phase region (Sol+Liq) on the high pressure side from a three phase region (Sol+Liq+Gas) on the low pressure side. Reservoir systems plotting in the two-phase region are described as "undersaturated" with methane (i.e. the total system pressure is greater than the equilibrium vapor pressure of methane). Reservoirs plotting in the three-phase field are described as "oversaturated" with methane (i.e. there is sufficient methane present to form a distinct gas phase). A reservoir that initially plots in the two-phase region will form a distinct gas phase at the bubble point pressure, i.e. the point at which the P-X pathway encounters the isotherm curve. In contrast with typical production models, as reservoir pressure continues to decrease, the P-X pathway will cross the isotherm into the three-phase field, as some proportion of the porosity becomes

filled with the gas phase. In classic CBM production models, the gas phase forms only within the fracture system, not within the matrix. There is no reason, however, why a gas phase will not form wherever it is thermodynamically favored, even with the matrix. Evidence from the Antrim Shale and Powder River Basin (CBM) suggests that as the gas phase forms and expands, it can expel interstitial water from the matrix, resulting in excess water production. In principle, the same phenomenon could also cause expulsion of petroleum liquids, if present. The changing phase composition of the reservoir will substantially influence both sorption capacity and diffusion behavior.

It is fundamentally impossible to produce a free gas phase without simultaneously producing desorbed gas from the sorbed phase. Depending on the isotherm shape, the proportion of free gas and desorbed gas will vary with pressure. If pressure gradients within the formation are high, as would be expected in very low permeability shales, the sorbed gas contribution may be substantial, even during early phases of production.

At least three distinct processes may cause a net increase in reservoir porosity during production that may be occupied by the free gas phase: 1) As a gas phase forms and expands, it may displace liquids from the porosity, 2) The volume occupied by the sorbed phase at higher pressure will become available to the gas phase at lower pressure, and 3) Owing to the phenomenon of matrix shrinkage, the molar volume of the sorbent decreases as sorbate diffuses out of its structure. Production of desorbed gas retained in the porosity will be delayed until pressure is further reduced. Each of these phenomena should be incorporated into an accurate model of the reservoir.