

WHY LIGHT HYDROCARBONS DO NOT FORM A GAS PHASE AFTER DIFFUSING THROUGH SEALS

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INTRODUCTION

Gas diffusion through seals has been proposed to explain two phenomena: isotopically depleted, dry gases in conventional gas accumulations, and shortened life of gas accumulations. Some geochemists (e.g., Prinzhofer et al. 2000) believe that many isotopically depleted, dry gases are results of diffusive fractionation through seals. Kinetically fractionated gases can form conventional accumulations only where gas forms and migrates, so formation of a gas within and above the seal is essential. If gas remains in solution after diffusion, then it cannot migrate to shallower accumulations.

The purpose of this document is to show why formation of a gas from hydrocarbons which have diffused through a seal is unlikely or impossible in most geological settings.

BACKGROUND CONCEPTS

We will look at two issues, the diffusion process and the process of formation of a gas from dissolved light hydrocarbons.

The diffusive flux is proportional to the effective diffusivity and to the negative of the concentration gradient of the diffusing species (Fick's first law; e. g. Welty et al., 1969). During one dimensional, vertical diffusion of a hydrocarbon dissolved in pore water, the hydrocarbon accumulates if the vertical diffusive flux decreases upwards in the zone (as described by Fick's second law; Welty et al., 1969). Effective diffusivities are fixed for a given problem, but concentration gradients change with time as dissolved gases diffuse. If the range of concentration gradients

corresponding to different effective diffusivities can be identified, then conditions where dissolved methane can accumulate sufficiently to form a gas phase can be identified.

Concentration of the diffusing hydrocarbons will be expressed as partial pressure, the mole fraction of a gas phase multiplied by the total gas pressure (Welty et al. 1969). This can be done because light hydrocarbon concentration in water is proportional to its fugacity as described by Henry's law (Garrels and Christ 1965). Ideal gas behavior will be assumed, so fugacity is approximated by partial pressure. At the temperatures and pressures of interest, gas does not behave ideally. However, pressure and temperature change over the thickness of the seal are not likely to be significant, so deviations from ideal behavior will be approximately the same at all points on the diffusion pathway.

Ideal gas behavior is assumed, so a gas forms where the sum of the partial pressures equals the fluid pressure in the absence of capillary effects (Dalton's Law; Welty et al. 1969). The term "gas" refers to a phase, not a composition. "Methane" or "light hydrocarbon" refers to chemical species. Unless compositional effects are addressed, methane is assumed to be the only dissolved hydrocarbon species, so a gas phase will form where the methane partial pressure equals the total pressure in the absence of capillary effects. Likewise, methane gas will not be present if the methane partial pressure is less than the total pressure.

The pressure difference between gas and water in a reservoir is the capillary pressure.

The hydrocarbon capillary pressure is the difference between the partial pressure of the hydrocarbon and the pressure required to form a gas phase under conditions of interest. Undersaturated water therefore has a negative hydrocarbon capillary pressure. The term "capillary displacement pressure" is the capillary pressure necessary to form a gas which can migrate through the pore system. Where the hydrocarbon capillary pressure is less than the capillary displacement pressure, any exsolved gas is immobile, so the rock acts as a seal.

REASONS WHY GAS DOES NOT FORM ABOVE THE SEAL

There are three reasons why exsolution of gas diffused through a seal is unlikely in most geological settings. (1) A mobile gas cannot form in an intact, homogeneous seal, so the diffusive path must be at least as long as the seal thickness. (2) Methane diffuses through overlying strata as well as through the seal, and losses may prevent gas formation. (3) Diffusive compositional fractionation reduces the methane partial pressure below that necessary for gas formation, even after diffusive equilibration.

Gas Formation In The Seal

The thinner the seal, the steeper the concentration gradient across the seal and the faster the diffusion. For this reason, it has been proposed that gas forms near the base of the seal instead at the top of the seal (e. g., Prinzhofer et al., 2000). However, a migratable gas cannot form in a homogeneous seal, so the diffusion path must be at least as long as the seal is thick. To understand why this is so, the water pressure and methane partial pressure distribution in the seal need to be reviewed.

Water pressure at the base of the seal is controlled by pressure of overlying water. Shale seals are permeable to water, but gas reservoirs at irreducible water saturation are not. Water flow in the seal is caused only by its slow compaction, so its water pressure gradient (G) is approximately hydrostatic.

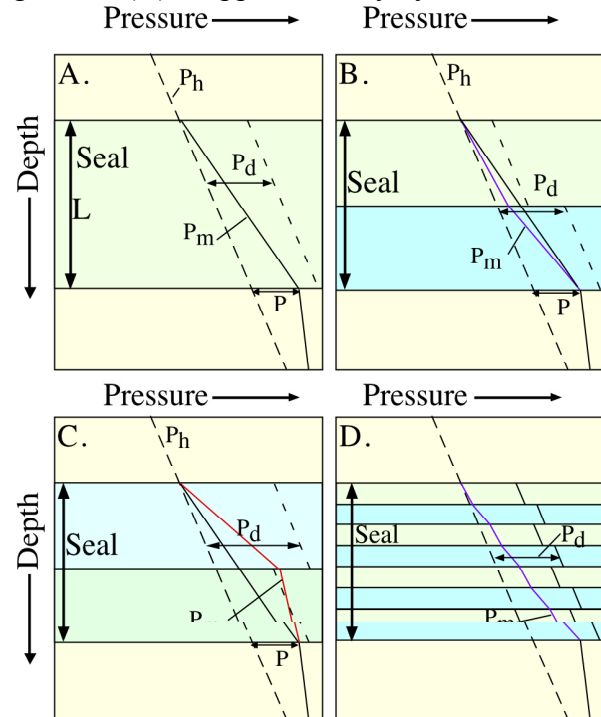


Figure 1. Methane partial pressure in seals at steady diffusion. A. Homogeneous seal. Maximum capillary pressure occurs at the base of the seal and decreases up section. B. Two layer heterogeneous seal, where the lower seal layer has lower diffusivity. P_m is lower than the single layer case. C. Two layer heterogeneous seal, where the lower layer has higher diffusivity. P_m is higher than the single layer case, and may exceed P_d of the lower layer. D. As the number of alternating higher and lower diffusivity layers increase, deviations from the average P_m trend are less, so it is less likely for P_m to exceed the capillary displacement pressure.

If the seal is homogeneous, its effective diffusivity and capillary displacement pressure is the same at all depths. The maximum methane concentration develops under steady diffusion in equilibrium with a reservoir capillary pressure. If gas is present at hydrostatic pressure at the top of the seal, the

methane partial pressure gradient is $G + P/L$, where L is the thickness of the seal and P is the capillary pressure at the base of the seal (Figure 1A). Under the most favorable conditions of steady diffusion and a positive P , methane capillary pressure decreases up section, because $G + P/L > G$. Because the seal is intact, the capillary pressure at the base of the seal is less than its capillary displacement pressure (P_d). The capillary pressure decreases up section, whereas the displacement pressure does not, so a gas phase cannot form in the seal.

Heterogeneous seals can be broken into a series of two-layer models, where the upper layer has either greater or lower diffusivity than the lower seal layer. Where the lower seal layer has lower diffusivity, methane capillary pressure is less than that of the single layer case (Figure 1B). Where the upper seal layer has lower diffusivity, methane capillary pressure is greater than that of the single layer case and may exceed the displacement pressure (Figure 1C). However, gas would form below the upper seal and could not migrate through it, because capillary displacement pressure of the upper layer is likely to be higher than that of the underlying layer. As more layers are added to the model, deviations from the single layer model become less, so it becomes less likely for the methane capillary pressure to exceed the displacement pressure (Figure 1D).

Mass balance during diffusion

Diffusion delivers dissolved light hydrocarbons to strata above porous seals, but diffusion also removes light hydrocarbons by continued upwards diffusion above the seal.

Assume that methane is the only light hydrocarbon diffusing upwards from a lower reservoir through a seal into an upper sandstone interval (Figure 2). The reservoir gas is 100 % methane at a fixed overpressure

(capillary pressure) P above seal hydrostatic pressure. The seal is a homogeneous, porous shale with thickness L . The overlying sandstone has water-filled porosity and zero capillary displacement pressure. The hydrostatic pressure gradient is G . Shale and upper sandstone effective diffusivities (D_{sh} and D_{ss} , respectively) are constant in each layer.

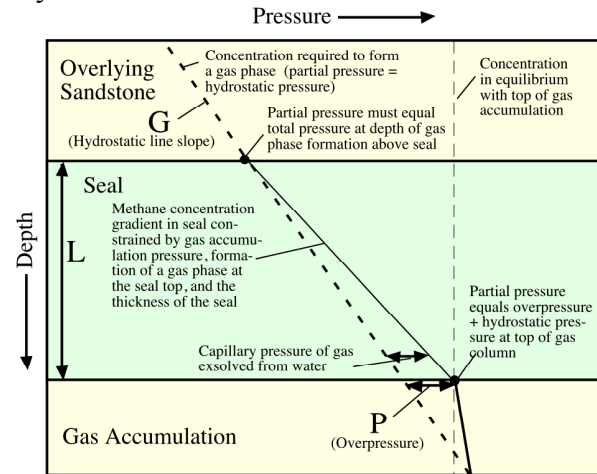


Figure 2. Concentration (as partial pressure) vs. depth for steady diffusion of methane through a seal where a gas phase forms above the seal. Methane concentration gradient in the seal is controlled by the pressure in the underlying gas reservoir, the requirement to form a gas phase above the seal, and the thickness of the seal. The minimum possible methane partial pressure gradient in the overlying sandstone is the hydrostatic gradient G if water is gas-saturated at the seal-sandstone interface.

The reservoir layer forms the lowest boundary for diffusion through the seal. Methane must diffuse through the entire seal thickness before a gas phase can form, because its capillary displacement pressure is high. The partial pressure of dissolved methane at the top of the seal and in the overlying sandstone is assumed to equal the water pressure. Under these conditions, any additional methane accumulation above the seal will lead to gas formation.

If the water at the top of the seal is methane-saturated, then the maximum possible partial pressure gradient at the top of the seal is the pressure difference between the

top of the gas reservoir and the base of the overlying sandstone divided by the thickness of the seal (i.e., $G + P/L$; see Figure 2). This gradient is equal to the steady diffusion gradient through the homogeneous seal.

The conditions under which gas exsolves can now be evaluated given the most favorable concentration gradients, maximum gradient into the base of the sandstone and minimum gradient away from the base of the sandstone. If a gas phase does not form under these conditions, it will not form under any conditions. Gas concentration doesn't change where the flux in and out are the same: $-D_{sh}^* (G + P/L) = -D_{ss}^* G$. (negative indicates upwards flux, L is positive downward). This can be rearranged to relate the ratio of the effective diffusivity to the ratio of the concentration gradients: $D_{sh}/D_{ss} = G/(G + P/L)$. For gas to form, the flux upwards into the base of the sandstone must exceed the flux through the sandstone, so the ratio of shale effective diffusivity to sandstone effective diffusivity must exceed the ratio of the concentration gradients:

$$D_{sh}/D_{ss} > G/(G + P/L). \quad (1)$$

There are three ranges of solutions to this inequality (Figure 3). First, if the reservoir methane pressure is less than the water pressure above the seal ($L < |P/G|$ and $P < 0$), gas diffusion upwards through the seal to form a gas is impossible because this would require a negative diffusivity, which is impossible.

Second, if the reservoir methane pressure is greater than the water pressure above the seal and the overpressure is negative ($L > |P/G|$, and $P < 0$), the effective diffusivity of the seal must be greater than the effective diffusivity of the overlying bed for gas to accumulate ($D_{sh}/D_{ss} > 1$). Whereas this is theoretically possible, shale seal effective diffusivities are experimentally determined to

be lower than those of poor quality sandstones or silts (Krooss, 1986). If this is true for all seals and overlying coarser-grained strata, gas formation above the seal is not possible under these conditions, either. Finally, where the overpressure is positive, it is possible to exsolve a gas above the seal with shale diffusivity less than that of sandstone ($D_{sh}/D_{ss} < 1$).

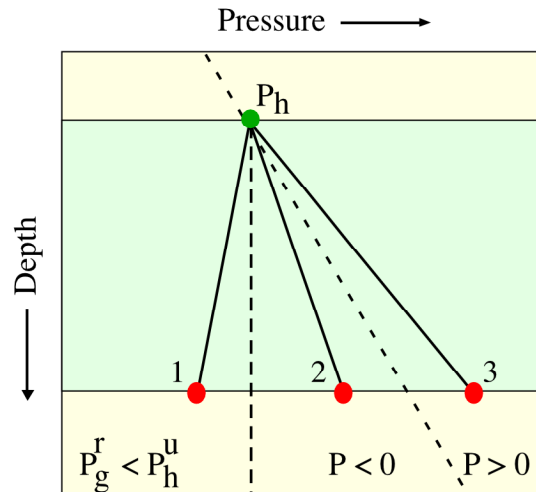


Figure 3. Possible relationships between reservoir gas pressure and hydrostatic pressure above the seal where the gas must exsolve. (1) If the reservoir gas pressure is less than the hydrostatic pressure above the seal, diffusion upwards through the seal is impossible. (2) If reservoir pressure is higher than the hydrostatic pressure at the top of the seal, but the overpressure is negative formation of a gas phase requires that diffusivity of the seal exceed that of the rock over the seal, which is inconsistent with experimental data and theory. (3) If the overpressure is positive, then formation of a gas phase is possible where the ratio of the seal to sandstone diffusivity is less than the ratio of the seal to sandstone concentration gradients.

As P/L increases, the effective diffusivity ratio required to form a gas above the seal decreases (Figure 4). The following conditions are typical for a typical small gas accumulation: P is 0.2 MPa (about 25 m gas column), G is 0.01 MPa/m (water density of 1 g/cc), and L is 100 m. Under these conditions, D_{sh}/D_{ss} is less about 0.83. In contrast, Krooss et al. (1988) interpret

permeable sandstone effective diffusivity to be about 100 times greater than the effective diffusivity of shale ($D_{sh}/D_{ss} \approx 0.01$). Assuming that shale effective diffusivity is one hundredth the sandstone effective diffusivity, overpressure of about 10 MPa and 100 MPa would be required to form a gas phase above a 10 and 100 m seal, respectively. A 10 MPa overpressure is created by a gas column about 1.2 km tall, whereas a 100 MPa overpressure is created by a gas column 12 km tall.

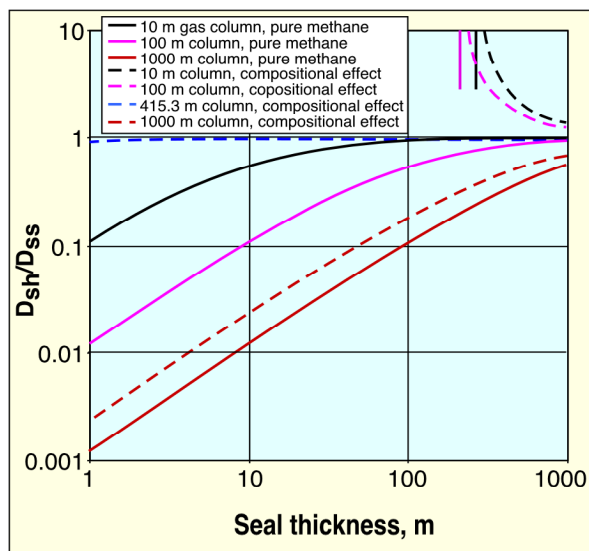


Figure 4. Calculated relative diffusivity necessary to form a gas phase above a seal with and without gas compositional effects. Under the conditions assumed here, a gas column of at least 415.3 m is required for $D_{sh}/D_{ss} < 1$ where compositional differences affect diffusion. Assumed conditions are hydrostatic pressure gradient, reservoir depth of 3 km, gas density of 0.15 g/cc, and methane fraction of 0.85 in the reservoir gas and 0.95 in the gas exsolved above the seal. Gas columns of 10, 100, and 1000 m create capillary pressures of 0.085, 0.85, and 8.5 MPa, respectively.

Effects of compositional variation

Because methane is more soluble and has a faster diffusivity than heavier hydrocarbons, gas exsolved from water above the seal will be drier than gas in the reservoir. This

decreases the likelihood for forming gas above the seal. If a reservoir gas is wet, its methane partial pressure is considerably less than the total pressure. Dry gas exsolved above the seal will have methane partial pressure closer to the total pressure. The methane partial pressure gradient must be less than the total pressure gradient, so methane diffusion through the seal is slower. However, concentration gradients in beds overlying the seal do not decrease, so diffusive loss does not decrease. As a result, it is more difficult to form a gas above the seal.

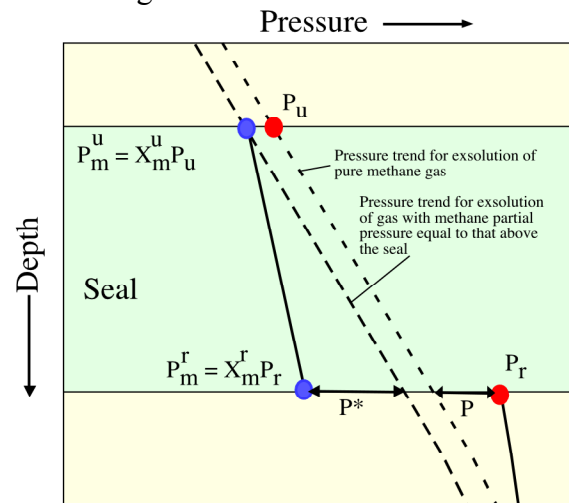


Figure 5. Methane partial pressures (blue circles) where exsolved gas is drier than the reservoir gas. The difference in methane partial pressure is less than the difference in total pressure (red circles). The methane partial pressure of a wet gas in the reservoir may be less than that of exsolved gas above the seal. In this example, the total gas overpressure (P) is positive, but the methane gas overpressure (P^*) is negative.

The compositional effect can be incorporated into a corrected methane overpressure (P^*) which can be used with Equation 1 to calculate the diffusivity ratio required for gas formation. Consider the same reservoir-seal-sandstone geometry of Figure 2, only now consider the compositional change of the gas after it diffuses across the seal (Figure 5). Methane diffusion is controlled by the gradient in the methane partial pressure. Instead of methane gas exsolution at the

hydrostatic pressure line, gas exsolves where the methane partial pressure is equal to that of the exsolved gas: $P_m^r = X_m^t P_h$, which will be less than the total pressure. The corrected methane overpressure is the pressure difference between the methane partial pressure in the reservoir (P_m^r) and methane partial pressure of an exsolved gas above the seal corrected for the difference in depth to the base of the reservoir: $P_m^r = X_m^t P_h^r + GL$. Hydrostatic pressure at the reservoir level, P_h^r is equal to $G(Z+L)$, while hydrostatic pressure above the seal is GZ . From these relationships, the corrected methane overpressure (P^*) is the following.

$$P^* = PX_m^r - G(Z+L)(X_m^t - X_m^r) + (1 - X_m^t)GL \quad (2)$$

Z is the depth to the top of the seal and X_m is the mole fraction methane in gas at the top of seal (t) and in the reservoir (r). The corrected methane overpressure (P^*) is substituted for P in Equation 1.

Even modest compositional changes result in negative methane overpressure where L is small especially where the reservoir is at great depth (Figure 4). In many cases, the methane partial pressure is less than that of a methane-rich gas which must exsolve above the seal, so diffusion cannot lead to gas formation.

These effects are shown in Figure 4, calculated from hydrostatic pressure gradient at 3 km depth, 85 % methane in the reservoired gas, and 95% methane in the exsolved gas. Short vertical lines in the upper right part of Figure 4 mark minimum seal thicknesses necessary for forming a gas phase without negative diffusivity ratios for 10 and 100 m gas columns. Gas formation above seals thicker than these require $D_{sh}/D_{ss} > 1$. Only where the gas column is over 415 m thick does D_{sh}/D_{ss} become less than 1. In contrast, all gas columns without

compositional effects and with positive P have $D_{sh}/D_{ss} < 1$.

Where low methane concentration in the reservoir is combined with high dissolved methane concentration in surrounding pore water, diffusive loss from the reservoir may stop as the concentration gradient drops to zero. This would be especially effective in very wet gases and undersaturated oils. It is even possible that methane dissolved in pore water may diffuse towards the accumulation instead of away from it (e. g., Montel et al. 1993).

WHERE CAN GASES EXSOLVE?

Available experimental data indicate that shale effective diffusivity is substantially lower than that of sandstones and siltstone, so gas formation above the seal is almost impossible in most settings. Based on Equations 1 and 2, gas columns hundreds to thousands of meters thick, seals less than 10 m thick, and very dry reservoired gases are needed to form a gas above the seal, if diffusivity ratios similar to experimental values are chosen. These conditions are rare, so settings where diffusion by itself forms a gas above seals are expected to be rare.

Special circumstances may be imagined where the seal/sandstone effective diffusivity ratio is significantly larger than 0.01. The easiest way is to decrease the reservoir quality of the overlying unit, which will increase its tortuosity and decrease its effective diffusivity. However, this has the side effect of increasing the rock capillary displacement pressure, so higher gas partial pressure is required to form a mobile gas. If a mobile gas phase does not form, the diffusive path length increases, concentration gradient decreases and diffusive flux decreases. The net result of decreasing reservoir quality of beds overlying the seal is to thicken the seal.

Another possible setting is where beds overlying the seal are overlain by another seal which limits its diffusive loss. This problem is similar to the heterogeneous seal already considered. The shallower seal also has diffusive loss. Rate of diffusive loss through the shallow seal will be similar to that of the deep seal unless the shallower seal has a lower effective diffusivity or greater thickness. Except in cases of obvious thickness variations, it is difficult to judge which seal would have the higher diffusive loss. Decreasing temperature up section decreases diffusivity whereas greater porosity at shallower depths will increase effective diffusivity.

Of course, there are other geological settings in which dissolved gases can exsolve. The two most obvious are recently exhumed basins and areas of resurgent subsurface waters (e. g., Cramer et al., 1999). As total pressure decreases, light hydrocarbons dissolved in pore water exsolve, and gas can then migrate to fill traps. Both settings are easily recognized by the geologist, so areas with potential for diffused gases might be predicted even before sampling. Even in these settings, solubility fractionation of light hydrocarbons will probably exceed diffusive fractionation, because all exsolved gas will have fractionated during dissolution and exsolution, whereas only some of the exsolved gases will have diffused from reservoirs.

SUMMARY AND CONCLUSIONS

Three processes limit the formation of a mobile gas after diffusion in and through a seal. First, gas dissolved in seal pore water is insufficiently supersaturated to form a mobile gas due to capillary effects, so diffusive path length must be at least as great as the seal thickness. Second, diffusivity is generally higher in coarse-grained rocks than in seals,

so diffusive losses from the interval above the seal are likely to equal diffusive supply through the seal as partial pressures approaches saturation. If so, no gas forms. Third, compositional fractionation between reservoir and exsolved gases reduces the methane overpressure necessary for gas exsolution above the seal.

Unless confining pressure decreases, exsolution of large quantities of gas after diffusion only occurs under the rare circumstances of exceptionally tall gas columns (thousands of meters) and thin shale seals (<10 m). I am not aware of any field with the combination of features necessary to exsolve a gas above the seal. No mechanism yet proposed can cause exsolution of large quantities of gas after diffusion without major changes in confining pressure and temperature. For this reason, I find it difficult to interpret gas geochemical trends from conventional gas accumulations in continuously subsiding basins as products of diffusion modification during migration.

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