BRAVO TUTORIAL
NOTE ON THE FLASH EQUATIONS USED IN THE SIMULATION

1. System description

We consider a system with two phases, water and gas, which contains Neon, Helium, Carbon dioxide and water. Let us introduce some notations. We denote by n_c the number of components, that is, $n_c = 4$. For each component $i = 1, \ldots, n_c$, $c_{i\alpha}$ denotes the concentration in mole per liter in each phase $\alpha = g, w$. We use Henry's law which states that, at phase equilibrium, there exists a constant k_i which depends only on temperature such that

$$(1) \qquad \frac{p_i}{c_{i,w}} = k_i,$$

where p_i denotes the partial pressure. We introduce vector notations and denote by $\boldsymbol{p}$, $\boldsymbol{c}_\alpha$ the vectors with components p_i and $c_{i,\alpha}$, respectively. Then, (1) can be rewritten as

$$(2) \qquad \boldsymbol{p} = \boldsymbol{H}\boldsymbol{c}_l$$

where $\boldsymbol{H}$ denotes the diagonal matrix with coefficients $k_i(T)$ on the diagonal. Let V_g and V_l denote the volume of gas and water, respectively. We denote by $\boldsymbol{n}_\alpha$ the number of mole in each phase $\alpha = \{g, w\}$. Assuming that the gas follow the ideal gas law, we have

$$V_g \boldsymbol{p} = RT \boldsymbol{n}_g$$

so that

$$(3) \qquad \boldsymbol{p} = RT \boldsymbol{c}_g$$

The Gibbs free energy is given by

$$(4) \qquad G = \boldsymbol{n}_g \cdot \boldsymbol{\mu}_g + \boldsymbol{n}_l \cdot \boldsymbol{\mu}_l = \boldsymbol{n} \cdot \boldsymbol{\mu}$$

and the total volume is given by

$$(5) \qquad V = \left(\frac{\partial G}{\partial p} \right)_{\boldsymbol{n},T} = \boldsymbol{n} \cdot \frac{\partial \boldsymbol{\mu}}{\partial P}$$

and, as $\mu_{i,g} = \mu_{i,g}^0(T) + RT \ln(p_i)$ for an ideal gas, the gas volume is given by

$$(6) \qquad V_g = \frac{RT}{P} \boldsymbol{e} \cdot \boldsymbol{n}_g,$$

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where $\boldsymbol{e} = [1, 1, 1, 1]^t$. Here, P denotes the pressure of the system. Thus we obtain

$$(7) \qquad\qquad 1 = \frac{RT}{P} \boldsymbol{e} \cdot \boldsymbol{c}_g.$$

For an ideal liquid solution, we have

$$(8) \qquad\qquad \mu_{i,l} = \mu_{i,l}^0(P, T) + RT \ln(\frac{n_i}{n_t})$$

where n_t denotes the total number of moles in the liquid phase. If we denote

$$(9) \qquad\qquad \omega_i = \frac{\partial \mu_{i,l}^0(P, T)}{\partial P},$$

we can write V_l as

$$(10) \qquad\qquad V_l = \boldsymbol{\omega}_l \cdot \boldsymbol{n}_l.$$

If the water phase is incompressible, then ω_l is independent of the pressure P. For a given composition $\boldsymbol{N}$ (in mole), the total amount of each element contained in all phases is conserved so that we have

$$(11) \qquad\qquad V_g \boldsymbol{c}_g + V_l \boldsymbol{c}_l = \boldsymbol{N}.$$

The system of equations (2), (3), (7), (10), (11) gives us $3n_c + 2$ equations, which can be solved for the $3n_c + 2$ unknown: $\boldsymbol{c}_g$, $\boldsymbol{c}_l$, $\boldsymbol{p}$, V_l and V_g. By flash calculation, we refer to the computation of the solution to this system, for a given $\boldsymbol{N}$. We define

$$(12) \qquad\qquad \boldsymbol{\omega}_g = RT\boldsymbol{e}$$

and the flash system can be rewritten as: the conservation of mass equations

$$(13a) \qquad\qquad V_g \boldsymbol{c}_g + V_l \boldsymbol{c}_l = \boldsymbol{N},$$

the equilibrium equations

$$(13b) \qquad\qquad \boldsymbol{H}\boldsymbol{c}_l = RT\boldsymbol{c}_g,$$

and the gas ans water volumes definitions

$$(13c) \qquad\qquad \boldsymbol{\omega}_g \cdot \boldsymbol{c}_g = P,$$

$$(13d) \qquad\qquad \boldsymbol{\omega}_l \cdot \boldsymbol{c}_l = 1,$$

for the unknown $\boldsymbol{c}_\alpha$ and V_α. Let us now find the condition for a single water phase equilibrium. First, we rewrite the flash system (13) in terms of mole number and obtain

$$(14a) \qquad\qquad \boldsymbol{n}_g + \boldsymbol{n}_l = \boldsymbol{N}$$

$$(14b) \qquad\qquad V_g \boldsymbol{H}\boldsymbol{n}_l = V_l RT \boldsymbol{n}_g$$

$$(14c) \qquad\qquad \boldsymbol{\omega}_g \cdot \boldsymbol{n}_g = PV_g,$$

$$(14d) \qquad\qquad \boldsymbol{\omega}_l \cdot \boldsymbol{n}_l = V_l.$$

Then, we observe that, for given N and total volume V, a trivial solution to (14) is the single water phase solution given by $\boldsymbol{n}_g = 0$, $V_g = 0$, $\boldsymbol{n}_l = \boldsymbol{N}$. If the water is compressible, then the pressure is computed by solving

$V = \boldsymbol{\omega}_l(P) \cdot \boldsymbol{N}$. If the water is incompressible, the pressure must be given. However, this solution is not stable if there exists a set of gas concentration $\boldsymbol{c}_g$ such that

$$(15) \qquad \boldsymbol{c}_g < \frac{1}{VRT}\boldsymbol{HN}$$

where the inequalities hold for each component. Indeed, if (15) holds a system with a gas phase with composition $\boldsymbol{c}_g$ is thermodynamically favored with respect to the single phase water solution. From (13a), we get that (15) is equivalent to

$$(16) \qquad \boldsymbol{\alpha}_g > 0,$$

where we define $\boldsymbol{\alpha}_g = \frac{1}{VRT}\boldsymbol{HN} - \boldsymbol{c}_g$. Since $\boldsymbol{c}_g$ also satisfies (13c), we require that

$$(17) \qquad \boldsymbol{\omega}_g \cdot \boldsymbol{\alpha}_g = \frac{1}{VRT}\boldsymbol{\omega}_g \cdot \boldsymbol{HN} - P.$$

We denote by β the right-hand side in (17). Since $\boldsymbol{\omega}_g > 0$, if there exists $\boldsymbol{\alpha}_g$ such that (16) holds, we must have $\beta > 0$. Conversely, if $\beta > 0$, then $\boldsymbol{\alpha}_g = \frac{\beta}{\|\boldsymbol{\omega}_g\|^2}\boldsymbol{\omega}_g$ satisfies both (16) and (17). Therefore the single water phase system is unstable if and only if

$$(18) \qquad P < \frac{1}{V}\boldsymbol{e} \cdot \boldsymbol{HN}.$$

We introduce the total concentration, defined as

$$\boldsymbol{C} = \frac{1}{V_g + V_l}\boldsymbol{N}.$$

We rewrite the flash equation for a given volume and obtain

$$(19a) \qquad\qquad S_g\boldsymbol{c}_g + S_l\boldsymbol{c}_l = \boldsymbol{C},$$
$$(19b) \qquad\qquad \boldsymbol{H}\boldsymbol{c}_l = RT\boldsymbol{c}_g,$$
$$(19c) \qquad\qquad \boldsymbol{\omega}_g \cdot \boldsymbol{c}_g = P,$$
$$(19d) \qquad\qquad \boldsymbol{\omega}_l \cdot \boldsymbol{c}_l = 1,$$
$$(19e) \qquad\qquad S_l + S_g = 1.$$

where the unknown are now P, $\boldsymbol{c}_\alpha$, S_α. The instability condition for the single water phase is

$$(20) \qquad\qquad P < \boldsymbol{e} \cdot \boldsymbol{HC}.$$

2. Adding Water vapor pressure

The water vapor pressure is a function of temperature alone and is well-approximated by

$$(21) \qquad p_{wg} = \exp\left(20.386 - \frac{5132}{T}\right) \text{mmHg}$$

where T is given in Kelvin. The system of equations (19) is then rewritten as

$$(22a) \qquad S_g \boldsymbol{c}_g + S_l \boldsymbol{c}_l = \boldsymbol{C},$$

$$(22b) \qquad S_g c_{wg} + S_l c_{wl} = C_w,$$

$$(22c) \qquad \boldsymbol{H}\boldsymbol{c}_l = RT\boldsymbol{c}_g,$$

$$(22d) \qquad RT c_{wg} = p_{wg}$$

$$(22e) \qquad \boldsymbol{\omega}_g \cdot \boldsymbol{c}_g + RT c_{wg} = P,$$

$$(22f) \qquad \boldsymbol{\omega}_l \cdot \boldsymbol{c}_l + \omega_{wl} c_{wl} = 1,$$

$$(22g) \qquad S_l + S_g = 1.$$

Using (22a), (22c) and (22g), we get that

$$c_{i,g} = \frac{C_i}{1 + (\frac{RT}{k_i} - 1)S},$$

where we denote by S the liquid saturation S_l Plugging this equation into (22e), we get

$$(23) \qquad \sum_{i=1}^{n_c} \left(\frac{RTC_i}{\frac{RT}{k_i}S + (1 - S)} \right) + p_{wg} = P.$$

Given the pressure P, we solve (23) and compute S. Once S is known, we can recover all the other unknown variables. The function on the left-hand side in (23) is continuous because the denominator in the sum never vanishes, as a convex combination of $\frac{RT}{k_i}$ and 1. Since the function is continuous, there exists a solution for P between p_0 and p_1, which are the values obtained for $S = 0$ and $S = 1$, that is,

$$(24) \qquad p_0 = RT \sum_{i=1}^{nc} C_i + p_{wg}$$

and

$$(25) \qquad p_1 = \sum_{i=1}^{nc} (k_i C_i) + p_{wg}.$$

Solutions for P not belonging to this interval would exist only if the function defined in (23) as $P(S)$ admits an extremum in $[0, 1]$. We observe that the derivative

$$(26) \qquad \frac{dP}{dS} = \sum_{i=1}^{n_c} \frac{RTC_i(1 - \frac{RT}{k_i})}{\left(1 + (\frac{RT}{k_i} - 1)S\right)^2},$$

is always positive for ambient temperature or below, for the system under consideration in the Bravo simulation which contains He, Ne, CO_2.

3. The transport equations

We neglect capillary forces. Darcy's law give us for each flux

$$(27) \qquad \boldsymbol{v}_g = -\frac{k_{rg}}{\mu_g}\boldsymbol{K}(\nabla P - \rho_g g \nabla z),$$

$$(28) \qquad \boldsymbol{v}_l = -\frac{k_{rl}}{\mu_l}\boldsymbol{K}(\nabla P - \rho_l g \nabla z),$$

Then, the total mass conservation equations is given by

$$(29) \qquad \frac{\partial}{\partial t}(\phi\boldsymbol{C}) + \nabla \cdot (\boldsymbol{c}_g\boldsymbol{v}_g{}^{\mathsf{T}} + \boldsymbol{c}_l\boldsymbol{v}_l{}^{\mathsf{T}}) = \boldsymbol{q}$$

where ϕ denotes the porosity and $\boldsymbol{q}$ is a source term. There are $3n_c + 3$ unknown in the system

$$P, \ \boldsymbol{C}, \ \boldsymbol{c}_\alpha, \ S_\alpha$$

and the same number of equations, given by the flash equations (19) and the total mass conservation equations.