Example. What are the pH and composition of a solution made of $10^{-2.7}$ NaAc + $10^{-3.7}$ $NaHCO_3$ which then equilibrates with atmospheric CO_2?

Initial solution (prior to contact with gas), using HCO_3^- and Ac^- as components

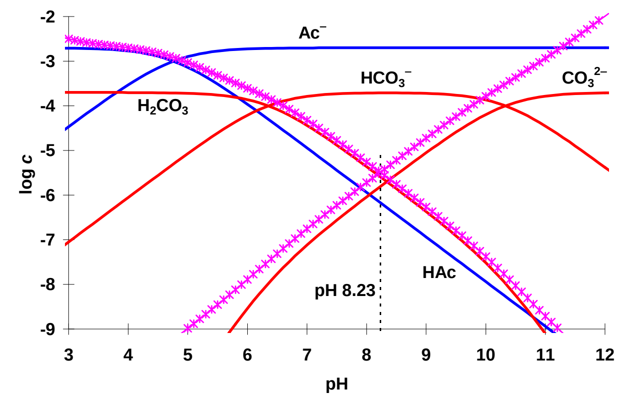
	H_2O	H^+	HCO_3^-	Ac^-	Na^+	log *K*	Conc'n
H_2O	1	0	0	0	0	0.00	
H^+	0	1	0	0	0	0.00	
HCO_3^-	0	0	1	0	0	0.00	
Ac^-	0	0	0	1	0	0.00	
Na^+	0	0	0	0	1	0.00	
OH^-	1	–1	0	0	0	–14.00	
HAc	0	1	0	1	0	4.74	
H_2CO_3	0	1	1	0	0	6.35	
CO_3^{2-}	0	–1	1	0	0	-10.33	
Inputs							
NaAc	0	0	0	1	1		$10^{-2.7}$
$NaHCO_3$	0	0	1	0	1		$10^{-3.7}$

$$0 + 0 = (H^+)_{eq} + (HAc)_{eq} + (H_2CO_3)_{eq} - (OH^-)_{eq} - (CO_3^{2-})_{eq}$$

$$(H^+) + (HAc) + (H_2CO_3) = (OH^-) + (CO_3^{2-})$$

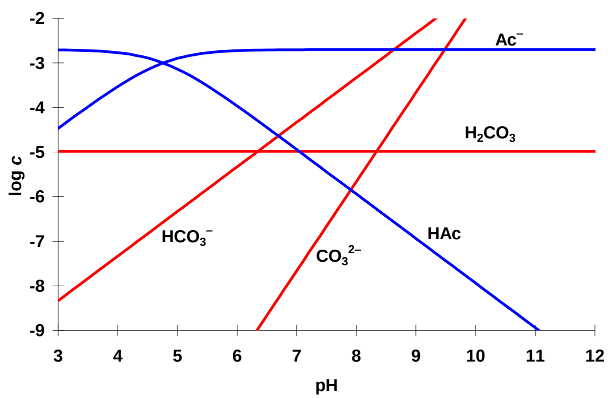
Initial Solution Composition

$$(H^+) + (HAc) + (H_2CO_3) = (OH^-) + (CO_3^{2-})$$



Gas-Liquid Equilibrium

Log c – pH Diagram After Equilibration with Atmosphere



$10^{-2.7}$ NaAc + $10^{-3.7}$ $NaHCO_3$ + equilibrium with atmospheric CO_2, still using HCO_3^- and Ac^- as components

	H_2O	H^+	HCO_3^-	Ac^-	Na^+	log *K*	Conc'n
H_2O	1	0	0	0	0	0.00	
H^+	0	1	0	0	0	0.00	
HCO_3^-	0	0	1	0	0	0.00	
Ac^-	0	0	0	1	0	0.00	
Na^+	0	0	0	0	1	0.00	
OH^-	1	–1	0	0	0	–14.00	
HAc	0	1	0	1	0	4.74	
H_2CO_3	0	1	1	0	0	6.35	**1.29×10^{-5}**
CO_3^{2-}	0	–1	1	0	0	-10.33	
Inputs							
NaAc	0	0	0	1	1		$10^{-2.7}$
$NaHCO_3$	0	0	1	0	1		$10^{-3.7}$
H_2CO_3	**0**	**1**	**1**	**0**	**0**		**??**

$$0+0+1(??) = (H^+)_{eq} + (HAc)_{eq} + (H_2CO_3)_{eq} - (OH^-)_{eq} - (CO_3^{2-})_{eq}$$

$$(H^+)_{eq} + (HAc)_{eq} + (H_2CO_3)_{eq} = (OH^-)_{eq} + (CO_3^{2-})_{eq} + ??$$

Same system, but using H_2CO_3 and Ac^- as components

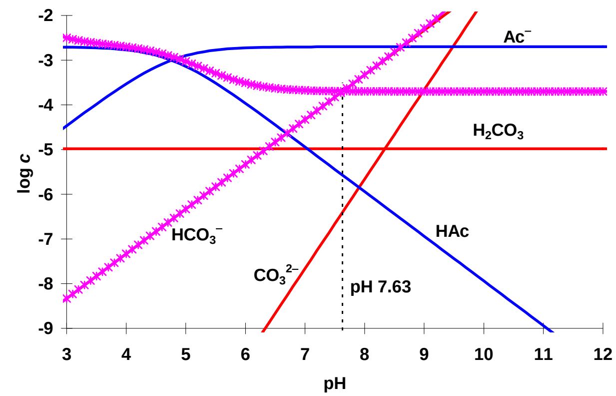
	H_2O	H^+	H_2CO_3	Ac^-	Na^+	log *K*	Conc'n
H_2O	1	0	0	0	0	0.00	
H^+	0	1	0	0	0	0.00	
H_2CO_3	0	0	1	0	0	0.00	1.29×10^{-5}
Ac^-	0	0	0	1	0	0.00	
Na^+	0	0	0	0	1	0.00	
OH^-	1	–1	0	0	0	–14.00	
HAc	0	1	0	1	0	4.74	
HCO_3^-	0	–1	1	0	0	-6.35	
CO_3^{2-}	0	–2	1	0	0	–16.68	
Inputs							
NaAc	0	0	0	1	1		$10^{-2.7}$
$NaHCO_3$	0	–1	1	0	1		$10^{-3.7}$
H_2CO_3	0	0	1	0	0		?

$$0 + (-1)10^{-3.7} + 0 = (H^+) + (HAc) - (OH^-) - (HCO_3^-) - 2(CO_3^{2-})$$

$$(H^+) + (HAc) + 10^{-3.7} = (OH^-) + (HCO_3^-) + 2(CO_3^{2-})$$

Gas-Liquid Equilibrium

After equilibration with atmosphere, using H_2CO_3 as component



Gas-Liquid Equilibrium

- *At initial condition,* $(H_2CO_3) \approx 10^{-5.4}$*, so solution was undersaturated, and* CO_2 *dissolved when the solution equilibrated with the atmosphere*
- *Final composition could have been found directly; determination of initial composition was informative, but not necessary*
- *Amount of* CO_2 *that dissolved can be computed as* $TOTCO_{3,fin} - TOTCO_{3,init} = 6.0 \times 10^{-4}$ *mol/L*
- *If the amount of a species that enters or leaves solution is unknown, that uncertainty can be circumvented by choosing the species as a component in the TOTH equation*

Gas-Liquid Equilibrium

- *Buffering by acidic or basic gases*
  - *When an acid is added to a solution containing an acidic neutral volatile species (e.g.,* CO_2*), the conjugate base (*HCO_3^-*) is converted to the acid, causing the acid to become supersaturated and evolve out of solution. If a base is added, the opposite reaction occurs, and the gaseous acid dissolves. If the dissolved neutral volatile species is a base (e.g.,* NH_3*), the reverse occurs.*
  - *In any of the above scenarios (acid or base added, acidic or basic volatile species), the net effect is that gas transfer partially counteracts acid or base addition. Therefore, the dissolved volatile species acts as a buffer.*
  - *The buffer intensity depends on the details of H and pH, which establish how much gas transfer occurs for a given change in pH*

Gas-Liquid Equilibrium

- *Alkalinity contributions by acidic or basic gases*
  - *Adding a weak base via gas dissolution is no different from adding it in some other way*
  - *H_2CO_3 addition or removal from solution has no effect on Alk, so dissolution or evolution of CO_2 also has no effect on Alk. Note that this result is independent of the solution pH. (The contribution of a species to pH always depends on the composition of what is added and the composition at the Alk endpoint, not on the speciation at intermediate times.)*