Gas-Liquid Equilibrium

- **Reaction and Equilibrium Constant Expression**

Dissolved volatile species ↔ *Gaseous volatile species*

$$K_{L\rightarrow G} = \frac{\{X(g)\}}{\{X(aq)\}} = \frac{\gamma_{X(g)}\left(c_{X(g)}/c_{X(g),std.state}\right)}{\gamma_{X(aq)}\left(c_{X(aq)}/c_{X(aq),std.state}\right)}$$

- $\gamma_{X(g)} \approx 1.0$ *because gases behave ideally*
- $\gamma_{X(aq)} \approx 1.0$ *because volatile species are uncharged*

Gas-Liquid Equilibrium

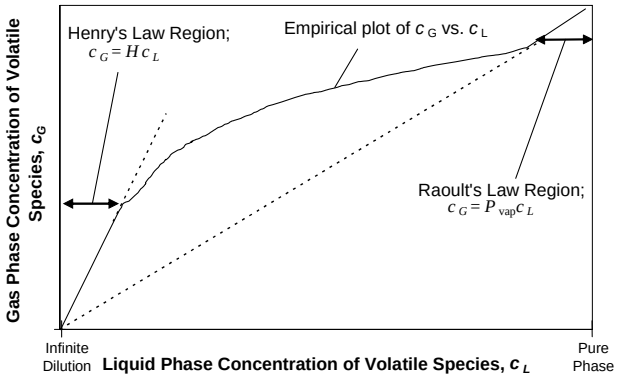
- *For major gaseous species,* $c_{X(g)}$ *typically expressed as* P_X, *and* $c_{X(g),std.state}$ *is 1.0 atm*

$$K_{L\rightarrow G} = \frac{(1.0)P_{X(g)}/(1\text{ atm})}{(1.0)c_{X(aq)}/(1\text{ mol/L})} = \frac{P_{X(g)}(\text{atm})}{c_{X(aq)}(\text{mol/L})}$$

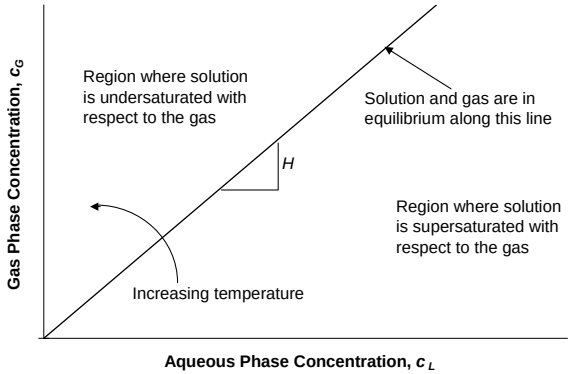
- *For minor species,* $c_{X(g)}$ *and* $c_{X(aq)}$ *often both expressed in same mass/volume units (e.g., mg/L or μg/L), and* $c_{X(g),std.state}$ *and* $c_{X(aq),std.state}$ *are 1.0 of same units*

$$K_{L\rightarrow G} = \frac{(1.0)c_{X(g)}/(1\text{ mg/L})}{(1.0)c_{X(aq)}/(1\text{ mg/L})} = \frac{c_{X(g)}}{c_{X(aq)}}$$

Gas-Liquid Equilibrium



Gas-Liquid Equilibrium



Gas-Liquid Equilibrium

$$c_{X(aq)} = \frac{P_{X(g)}}{H}$$

- *For equilibrium between a limited amount of gas and a limited amount of liquid, $P_{X(g)}$ decreases as $c_{X(aq)}$ increases; equilibrium is reached when K_H is satisfied.*

- *For equilibrium with an effectively infinite gas phase (e.g., the atmosphere), $P_{X(g)}$ remains constant when $c_{X(aq)}$ changes; equilibrium is reached when $c_{X(aq)}$ reaches a specified value.*

$$c_{X(aq)} = \frac{P_{X(g)}}{H} = constant$$

Gas-Liquid Equilibrium

- *For equilibrium at 20°C with the atmosphere:*

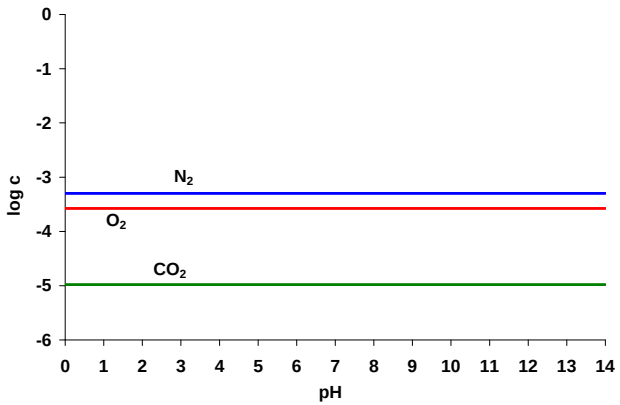
$$c_{N_2(aq)} = \frac{P_{N_2(g)}}{H_{N_2}} = \frac{0.79\ \text{atm}}{1560\ \text{atm/(mol/L)}}\left(\frac{28{,}000\ \text{mg}}{\text{mol}}\right) = 14.2\ \frac{\text{mg}}{\text{L}}$$

$$c_{O_2(aq)} = \frac{P_{O_2(g)}}{H_{O_2}} = \frac{0.21\ \text{atm}}{790\ \text{atm/(mol/L)}}\left(\frac{32{,}000\ \text{mg}}{\text{mol}}\right) = 8.5\ \frac{\text{mg}}{\text{L}}$$

$$c_{CO_2(aq)} = \frac{P_{CO_2(g)}}{H_{CO_2}} = \frac{10^{-3.5}\ \text{atm}}{30.2\ \text{atm/(mol/L)}} = 1.05\text{x}10^{-5}\ \frac{\text{mol}}{\text{L}}$$

Gas-Liquid Equilibrium

- *For equilibrium at 20°C with the atmosphere:*



Gas-Liquid Equilibrium

- *If the dissolved concentration of a volatile species is less than what would be in equilibrium with the existing partial pressure of that species in the gas phase, it will transfer from the gas to the solution (dissolve); if the dissolved concentration is greater than the value that would be in equilibrium with the partial pressure in the gas, the species will transfer out of solution (volatilize or evolve)*

- *Volatile species will volatilize passively (via diffusion across the interface) if the total partial pressure of all such species is less than the total pressure in the gas phase; gas bubbles will form in the liquid (e.g., fizzing of carbonated beverages or boiling of water) only if the total partial pressure of all dissolved species is greater than the total pressure on the solution*

Gas-Liquid Equilibrium

- *Equilibrium between and among dissolved species is **unaffected** by the fact that one of the species is equilibrated with the gas phase. In particular, K_a relationships must still be satisfied. But K_H must also be satisfied; e.g., for CO_2 (or, equivalently H_2CO_3) in equilibrium with the atmosphere:*

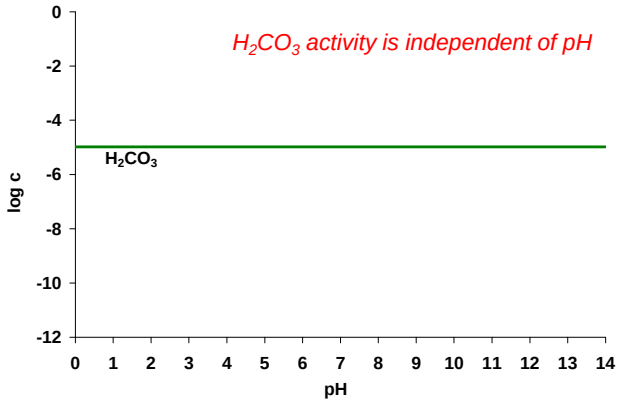
$$c_{CO_2(aq)} = 1.05\text{x}10^{-5}\ \frac{\text{mol}}{\text{L}}$$

H_2CO_3 activity is independent of pH

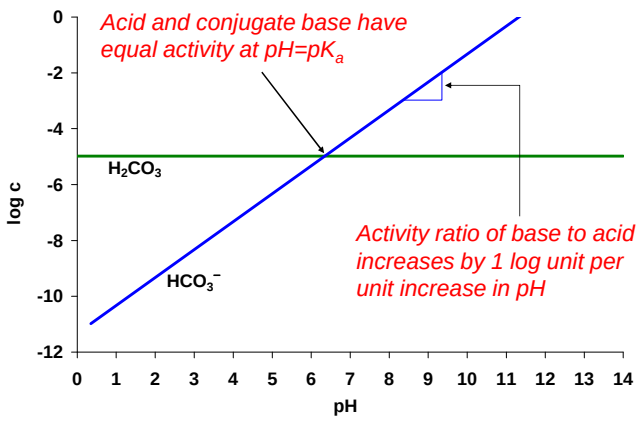
$$\left.\begin{aligned}\frac{(HCO_3^-)(H^+)}{(H_2CO_3)} &= 10^{-6.35}\\ \frac{(CO_3^{2-})(H^+)}{(HCO_3^-)} &= 10^{-10.33}\end{aligned}\right\}$$

Acid and conjugate base have equal activity at pH=pK_a; activity ratio of base to acid increases by 1 log unit per unit increase in pH

Gas-Liquid Equilibrium



Gas-Liquid Equilibrium



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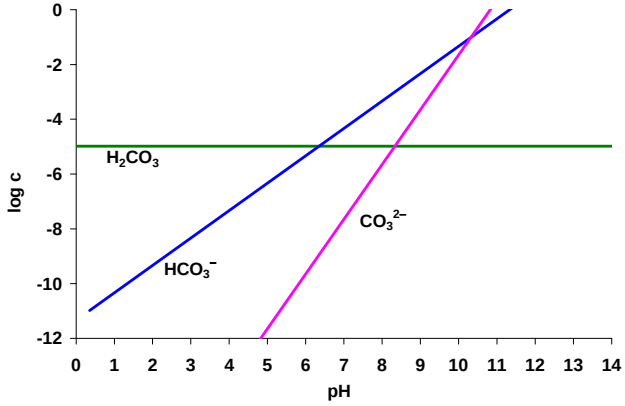

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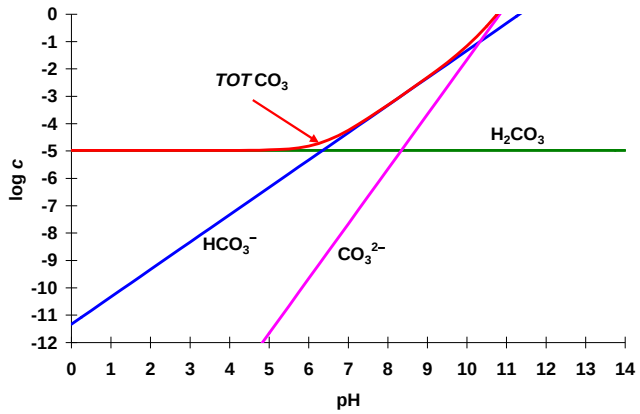


Gas-Liquid Equilibrium

- *As pH is increased, H_2CO_3 is converted to HCO_3^- and CO_3^{2-}, and more CO_2 dissolves to maintain Henry's Law equilibrium. $TOTCO_3$ therefore increases. Thus, in a system equilibrated with a gas containing CO_2, $TOTCO_3$ depends on pH, and we can't know $TOTCO_3$ without knowing pH.*

Example. What is the pH and composition of a solution of pure water in equilibrium with atmospheric CO_2?

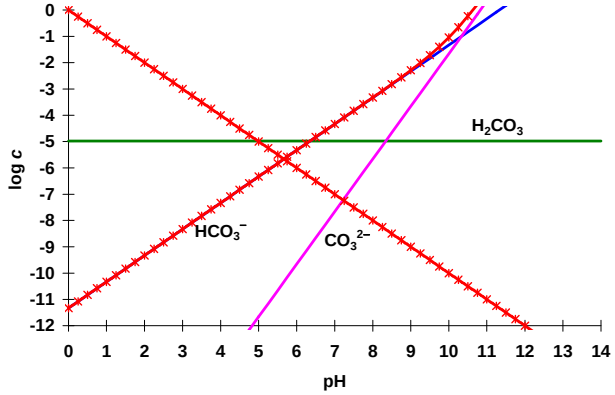
Unknowns: (H_2CO_3), (HCO_3^-), (CO_3^{2-}), (H^+), (OH^-)

Equations: K_w, K_{a1}, K_{a2}, CB, *H*

H replaces MB on $TOTCO_3$, since $TOTCO_3$ is unknown

Gas-Liquid Equilibrium

- CB: $(H^+) = (OH^-) + (HCO_3^-) + 2(CO_3^{2-})$



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

	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	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	
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		$10^{-3.7}$
H_2CO_3	0	1	1	0	0		??

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

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