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Here is a solution for Part A.

Part A. Nucleation, growth and rise of bubbles

A.1 Expression for the bubble pressure, P_b

I am observing a small bubble of gas within a liquid. This bubble is a distinct entity, a pocket of gas separated from the surrounding liquid by a spherical interface. This interface possesses a surface tension, denoted by σ. I conceive of this surface tension as an energy per unit area, or equivalently, a force per unit length acting along the surface. To maintain its spherical shape against this tension, which constantly tries to minimize the surface area and collapse the bubble, the pressure inside the bubble, P_b, must be greater than the pressure in the liquid just outside it, P_0.

To find the relationship between this excess pressure and the surface tension, I shall perform a thought experiment based on energy conservation. Let us imagine we infinitesimally increase the bubble's radius from a to $a + \text{d}a$.

The work, $\text{d}W$, done by the excess pressure, $\Delta P = P_b - P_0$, in expanding the bubble is the force it exerts multiplied by the distance the surface moves. The force is ΔP times the surface area, $4\pi a^2$. The distance is $\text{d}a$.
$$\text{d}W = (P_b - P_0) \cdot (4\pi a^2) \cdot \text{d}a$$

This work must be equal to the increase in the surface energy of the bubble, $\text{d}U$. The surface energy is the surface tension σ multiplied by the surface area $A = 4\pi a^2$.
$$U = \sigma (4\pi a^2)$$
The change in this energy is:
$$\text{d}U = \frac{\text{d}U}{\text{d}a} \text{d}a = \sigma (8\pi a) \text{d}a$$

By equating the work done to the change in surface energy, $\text{d}W = \text{d}U$, I find:
$$(P_b - P_0) \cdot (4\pi a^2) \cdot \text{d}a = \sigma (8\pi a) \text{d}a$$
Dividing both sides by $4\pi a \, \text{d}a$, a beautifully simple relationship emerges:
$$(P_b - P_0)a = 2\sigma$$
Solving for the pressure inside the bubble, P_b, I arrive at the expression:
$$P_b = P_0 + \frac{2\sigma}{a}$$
This confirms my initial hypothesis: the pressure inside is indeed greater than the outside pressure, and this excess pressure, $2\sigma/a$, becomes larger as the bubble radius a becomes smaller.

A.2 Critical radius for bubble growth, a_c

A bubble grows when CO_2 molecules diffuse from the liquid into the bubble. This diffusion is driven by a difference in concentration. The bulk liquid has a CO_2 concentration c_ℓ. The liquid immediately at the bubble's surface has a concentration c_b, which is in equilibrium with the pressure P_b inside the bubble, as described by Henry's Law: $c_b = k_H P_b$.

For the bubble to grow, there must be a net flow of CO_2 into it, which requires the concentration in the surrounding liquid to be higher than at the surface. Thus, the condition for growth is $c_\ell > c_b$.

A bubble is at a critical point, neither growing nor shrinking, when the concentrations are exactly balanced: $c_\ell = c_b$. Let us call the radius at this point the critical radius, a_c.
$$c_\ell = c_b = k_H P_b$$
Substituting my previously derived expression for P_b (with $a = a_c$):
$$c_\ell = k_H \left(P_0 + \frac{2\sigma}{a_c} \right)$$
$$c_\ell = k_H P_0 + \frac{2\sigma k_H}{a_c}$$
The problem defines the equilibrium concentration at atmospheric pressure as $c_0 = k_H P_0$. Substituting this gives:
$$c_\ell = c_0 + \frac{2\sigma k_H}{a_c}$$
Now, I can solve for the critical radius a_c:
$$c_\ell - c_0 = \frac{2\sigma k_H}{a_c}$$
$$a_c = \frac{2\sigma k_H}{c_\ell - c_0}$$

To calculate the numerical value, I am given that $c_\ell = 4c_0$. This means $c_\ell - c_0 = 3c_0$. Substituting this into my expression for a_c:
$$a_c = \frac{2\sigma k_H}{3c_0}$$
And since $c_0 = k_H P_0$, the Henry's constant k_H cancels out:
$$a_c = \frac{2\sigma k_H}{3k_H P_0} = \frac{2\sigma}{3P_0}$$
Using the provided values: $\sigma = 47 \times 10^{-3}$ J·m^{-2} and $P_0 = 1.0 \times 10^5$ Pa.
$$a_c = \frac{2 \cdot (47 \times 10^{-3} \text{ J m}^{-2})}{3 \cdot (1.0 \times 10^5 \text{ Pa})} = \frac{94 \times 10^{-3}}{3 \times 10^5} \text{ m} \approx 3.13 \times 10^{-7} \text{ m}$$
So, the critical radius is approximately **0.31 µm**. Any pre-existing gas cavity larger than this will spontaneously grow.

A.3 Bubble growth model and determination of the diffusion/transfer coefficient

First, I must find an expression for the number of moles of CO_2, n_c, inside the bubble. Assuming CO_2 behaves as an ideal gas, the ideal gas law applies: $P_b V = n_c R T_0$. The volume of the spherical bubble is $V = (4/3)\pi a^3$. The problem states that for visible bubbles, the excess pressure is negligible, so I can make the approximation $P_b \approx P_0$.

$$P_0 \left(\frac{4}{3}\pi a^3 \right) = n_c R T_0$$

Solving for n_c gives:

$$n_c = \frac{4\pi P_0 a^3}{3 R T_0}$$

The bubble grows as moles are transferred across its surface. The rate of change of moles, $\text{d}n_c/\text{d}t$, is the flux j (moles per area per time) multiplied by the surface area of the bubble, $4\pi a^2$.

$$\frac{\text{d}n_c}{\text{d}t} = j \cdot (4\pi a^2)$$

I can also find $\text{d}n_c/\text{d}t$ by differentiating my expression for n_c with respect to time:

$$\frac{\text{d}n_c}{\text{d}t} = \frac{\text{d}}{\text{d}t} \left(\frac{4\pi P_0 a^3}{3 R T_0} \right) = \frac{4\pi P_0}{3 R T_0} \cdot (3a^2) \frac{\text{d}a}{\text{d}t} = \frac{4\pi P_0 a^2}{R T_0} \frac{\text{d}a}{\text{d}t}$$

Equating the two expressions for $\text{d}n_c/\text{d}t$:

$$\frac{4\pi P_0 a^2}{R T_0} \frac{\text{d}a}{\text{d}t} = j \cdot (4\pi a^2)$$

The term $4\pi a^2$ cancels, leading to a direct relation between the growth rate of the radius and the flux:

$$\frac{\text{d}a}{\text{d}t} = \frac{R T_0}{P_0} j$$

Now I will test the two proposed models for the flux j. In both models, since $P_b \approx P_0$, the concentration at the surface is $c_b \approx k_H P_0 = c_0$.

- **Model (1):** $j = D(c_\ell - c_0)/a$ $$\frac{\text{d}a}{\text{d}t} = \frac{R T_0}{P_0} \left(\frac{D(c_\ell - c_0)}{a} \right)$$ This is a differential equation of the form $a(\text{d}a/\text{d}t) = \text{constant}$. Integrating with respect to time gives $\int a \, \text{d}a = \int \text{const} \, \text{d}t$, which yields $(1/2)a^2 = (\text{const})\cdot t$. Therefore, this model predicts $\boldsymbol{a(t) \propto \sqrt{t}}$.

- **Model (2):** $j = K(c_\ell - c_0)$ $$\frac{\text{d}a}{\text{d}t} = \frac{R T_0}{P_0} K(c_\ell - c_0)$$ In this case, the entire right-hand side is a constant. The differential equation is $\text{d}a/\text{d}t = \text{constant}$. Integrating gives $a = (\text{const})\cdot t$. This model predicts a linear relationship: $\boldsymbol{a(t) \propto t}$.

Now I must consult the experimental evidence. Figure 2 shows the bubble radius a as a function of time t. The data points form a clear straight line passing through the origin. This linear relationship is precisely what is predicted by **Model (2)**.

Having identified the correct model, I can now calculate the constant K. The slope of the graph in Figure 2 represents the constant growth rate, $\text{d}a/\text{d}t$. From the graph, I can see that at $t = 100$ s, the radius is $a = 400$ µm.

$$\frac{\text{d}a}{\text{d}t} = \frac{400 \times 10^{-6} \text{ m}}{100 \text{ s}} = 4.0 \times 10^{-6} \text{ m/s}$$

I can now solve for K using the growth rate equation from Model (2):

$$K = \frac{\text{d}a}{\text{d}t} \cdot \frac{P_0}{R T_0 (c_\ell - c_0)}$$

Given $c_\ell \approx 4c_0$, we have $c_\ell - c_0 = 3c_0 = 3k_H P_0$.

$$K = \frac{\text{d}a}{\text{d}t} \cdot \frac{P_0}{R T_0 (3k_H P_0)} = \frac{\text{d}a/\text{d}t}{3k_H R T_0}$$

The experiment is at $T_0 = 20$ °C $= 293.15$ K, where $k_H = 3.3 \times 10^{-4}$ mol·m^{-3}·Pa^{-1}.

$$K = \frac{4.0 \times 10^{-6} \text{ m/s}}{3 \cdot (3.3 \times 10^{-4} \text{ mol m}^{-3} \text{Pa}^{-1}) \cdot (8.314 \text{ J mol}^{-1} \text{K}^{-1}) \cdot (293.15 \text{ K})}$$

$$K = \frac{4.0 \times 10^{-6}}{2.417} \text{ m/s} \approx 1.65 \times 10^{-6} \text{ m/s}$$

A.4 Bubble velocity and liquid viscosity

A bubble rising vertically through the liquid is subject to several forces.

1. **Buoyant Force (upwards):** $F_b = \rho_\ell g_0 V$, *where* ρ_ℓ *is the liquid density and* V *is the bubble volume.* $$F_b = \rho_\ell g_0 \left(\frac{4}{3}\pi a^3\right)$$
2. **Drag Force (downwards):** Given by Stokes' law, $F_d = 6\pi\eta a v$.
3. **Gravitational Force (downwards):** $F_g = m_{bubble} g_0$. The mass of the CO_2 gas in the bubble is $m_{bubble} = \rho_{gas} V$. Since the density of the gas ($\rho_{gas} \approx 1.8$ kg·m^{-3}) is vastly smaller than the density of the liquid ($\rho_\ell = 1000$ kg·m^{-3}), this force is negligible compared to the buoyant force. I shall neglect it.

The problem states the bubble travels at its terminal velocity, which means the net force is zero. The upward buoyant force must balance the downward drag force.

$$F_b = F_d$$

$$\rho_\ell g_0 \left(\frac{4}{3}\pi a^3\right) = 6\pi\eta a v$$

I can now solve for the terminal velocity v as a function of the radius a:

$$v(a) = \frac{\rho_\ell g_0 (4/3)\pi a^3}{6\pi\eta a} = \frac{2 \rho_\ell g_0 a^2}{9\eta}$$

To estimate the dynamic viscosity η, I will use the data from Figure 3. The frequency of bubble emission is $f_b = 20$ Hz, meaning the time interval between successive bubbles is $\Delta t = 1/f_b = 0.05$ s. The distance between two consecutive bubbles, Δz, is the distance a bubble travels in this time. Thus, the velocity at that position is $v = \Delta z/\Delta t$.

From the image, I will select two adjacent bubbles in the middle of the train to make a measurement.

- The distance between their centers, Δz, appears to be approximately 1.5 mm, or 1.5×10^{-3} m.
- The velocity is then $v = (1.5 \times 10^{-3}\ \text{m}) / (0.05\ \text{s}) = 0.03$ m/s.
- The radius a at this point should be the average radius. The diameters appear to be around 0.5 mm and 0.7 mm, so I will estimate the average diameter as 0.6 mm, which gives a radius of $a \approx 0.3$ mm $= 3.0 \times 10^{-4}$ m.

Now, I rearrange my velocity expression to solve for η: [\eta = \frac{2 \rho_\ell g_0 a^2}{9v}] Substituting the values (using g0 = 9.8 m/s²): [\eta = \frac{2 \cdot (1.0 \times 10^3 \text{ kg m}^{-3}) \cdot (9.8 \text{ m s}^{-2}) \cdot (3.0 \times 10^{-4} \text{ m})^2}{9 \cdot (0.03 \text{ m/s})}] [\eta = \frac{2 \cdot 1000 \cdot 9.8 \cdot (9 \times 10^{-8})}{0.27} = \frac{1.764 \times 10^{-3}}{0.27} \text{ Pa}\cdot\text{s}] [\eta \approx 6.5 \times 10^{-3} \text{ Pa}\cdot\text{s}]

A.5 Bubble radius upon reaching the surface

The bubble grows as it rises. Its radius a and vertical position z are both functions of time t. I have two key relations:

1. The growth rate: $da/dt = qa$ (assumed constant)
2. The rise velocity: $dz/dt = v(a) = (2\rho\ell g0/9\eta)a^2 = Ca^2$, where C is a constant.

To relate the change in radius to the change in height, I use the chain rule: [\frac{\text{d}a}{\text{d}z} = \frac{\text{d}a/\text{d}t}{\text{d}z/\text{d}t} = \frac{q_a}{C a^2}] This is a separable differential equation. I can rearrange and integrate it from the bottom of the glass (*z*=0, *a*=*a*0) to the surface (*z*=*Hℓ*, *a*=*a*H*ℓ*). [a^2 \text{d}a = \frac{q_a}{C} \text{d}z] [\int_{a_0}^{a_{H\ell}} a^2 \text{d}a = \int_0^{H_\ell} \frac{q_a}{C} \text{d}z] [\left[\frac{1}{3}a^3 \right]*{a_0}^{a*{H\ell}} = \frac{q_a}{C} \left[z \right]*0^{H*\ell}] [\frac{1}{3} (a_{H\ell}^3 - a_0^3) = \frac{q_a H_\ell}{C}] The problem states to assume *aHℓ* ≫ *a*0, so *a*0³ is negligible. [\frac{1}{3} a_{H\ell}^3 \approx \frac{q_a H_\ell}{C} \implies a_{H\ell}^3 \approx \frac{3 q_a H_\ell}{C}] Substituting back the expression for C = (2*ρℓ*g0)/(9*η*): [a_{H\ell}^3 \approx \frac{3 q_a H_\ell}{(2\rho_\ell g_0)/(9\eta)} = \frac{27 q_a \eta H_\ell}{2 \rho_\ell g_0}] The final expression for the radius is: [a_{H\ell} = \left(\frac{27 q_a \eta H_\ell}{2 \rho_\ell g_0} \right)^{1/3}]

For the numerical value, I use:

- $H\ell = 10$ cm $= 0.1$ m
- $qa = 4.0 \times 10^{-6}$ m/s (from A.3)
- $\eta \approx 6.5 \times 10^{-3}$ Pa·s (from A.4)
- $\rho\ell = 1.0 \times 10^3$ kg·m^{-3}
- g0 = 9.8 m·s^{-2} [a_{H\ell}^3 \approx \frac{27 \cdot (4.0 \times 10^{-6}) \cdot (6.5 \times 10^{-3}) \cdot (0.1)}{2 \cdot (1.0 \times 10^3) \cdot 9.8} = \frac{7.02 \times 10^{-8}}{19600} \approx 3.58 \times 10^{-12} \text{ m}^3] [a_{H\ell} \approx (3.58 \times 10^{-12})^{1/3} \text{ m} \approx 1.53 \times 10^{-4} \text{ m}] The radius of a bubble reaching the surface is approximately **0.15 mm**.

A.6 Characteristic time for CO_2 concentration decay

The concentration of dissolved CO_2, $c\ell$, decreases because the CO_2 is transferred into the rising bubbles. The total number of moles in the liquid is *Nliq = cℓ(t)Vℓ. The rate of change of these moles is: [\frac{\text{d}(c*\ell V_\ell)}{\text{d}t} = V_\ell \frac{\text{d}c_\ell}{\text{d}t}] This rate must equal the negative of the total rate at which moles are removed by all bubbles. The rate of removal is the number of bubbles leaving the surface per second multiplied by the number of moles in each bubble as it leaves.

The number of bubbles leaving per second is the number of nucleation sites, *N*b, times the frequency of emission at each site, *f*b. The number of moles in a bubble reaching the surface, *nHℓ, depends on its radius aHℓ. [n*{H\ell} = \frac{P_0 V_{H\ell}}{R T_0} = \frac{P_0}{R T_0} \left(\frac{4}{3}\pi a_{H\ell}^3 \right)] From A.5, we found an expression for *aHℓ*³ that depends on the growth rate *qa*. And from A.3, the growth rate *qa* depends on the concentration *cℓ*: [q_a = \frac{\text{d}a}{\text{d}t} = K \frac{R T_0}{P_0} (c_\ell - c_0)] Substituting this into the expression for *aHℓ*³ from A.5: [a_{H\ell}^3 = \frac{27 \eta H_\ell}{2 \rho_\ell g_0} \cdot q_a = \frac{27 \eta H_\ell}{2 \rho_\ell g_0} \left(K \frac{R T_0}{P_0} (c_\ell - c_0) \right)] Now I assemble the full differential equation: [V_\ell \frac{\text{d}c_\ell}{\text{d}t} = - (N_b f_b) \cdot n_{H\ell} = -N_b f_b \left[\frac{P_0}{R T_0} \frac{4}{3}\pi a_{H\ell}^3 \right]] [V_\ell \frac{\text{d}c_\ell}{\text{d}t} = -N_b f_b \left[\frac{P_0}{R T_0} \frac{4}{3}\pi \cdot \frac{27 \eta H_\ell K R T_0}{2 \rho_\ell g_0 P_0} (c_\ell - c_0) \right]] Many terms cancel out (P_0, RT_0), which simplifies the equation considerably: [V_\ell \frac{\text{d}c_\ell}{\text{d}t} = -N_b f_b \left[\frac{4\pi}{3} \cdot \frac{27 \eta H_\ell K}{2 \rho_\ell g_0} \right] (c_\ell - c_0)] [V_\ell \frac{\text{d}c_\ell}

{\text{d}t} = - \left[\frac{18\pi N_b f_b \eta H_\ell K}{\rho_\ell g_0} \right] (c_\ell - c_0)] This is the differential equation for $c\ell(t)$. It is a first-order linear differential equation of the form $\mathrm{d}y/\mathrm{d}t = -y/\tau$, where $y = c\ell - c0$. The characteristic time τ is the inverse of the constant term multiplying y. [\frac{1}{\tau} = \frac{1}{V_\ell} \left[\frac{18\pi N_b f_b \eta H_\ell K}{\rho_\ell g_0} \right]] Therefore, the characteristic time τ for the decay of the CO_2 concentration is: [\tau = \frac{V_\ell \rho_\ell g_0}{18\pi N_b f_b K \eta H_\ell}]