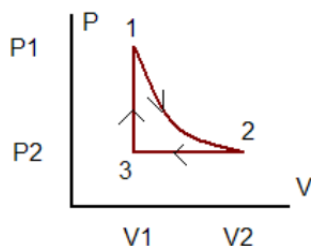


**Problem 1 – This Three Step Cycle Seems Familiar (40 points)**

a)



(4 pts for correct diagram)

b) Consider each path separately. The equations that we need are

$$\Delta U = nc_v \Delta T \quad (\text{any ideal gas})$$

$$w = \int -pdV$$

$$q_{\text{isotherm}} = -w$$

$$q_{\text{isobar}} = nc_p \Delta T$$

$$q_{\text{isochore}} = nc_v \Delta T$$

$$c_p = c_v + R \quad (\text{any ideal gas})$$

$$c_v = \frac{5}{2} R \quad (\text{ideal diatomic gas})$$

Along the isotherm (1-2):

$$q_{12} = nRT_1 \ln\left(\frac{V_2}{V_1}\right) = p_1 V_1 \ln\left(\frac{V_2}{V_1}\right) = p_1 V_1 \ln\left(\frac{p_1}{p_2}\right) \quad (\text{either answer is acceptable})$$

$$w_{12} = -nRT_1 \ln\left(\frac{V_2}{V_1}\right) = -p_1 V_1 \ln\left(\frac{V_2}{V_1}\right) = -p_1 V_1 \ln\left(\frac{p_1}{p_2}\right) \quad (\text{either answer is acceptable})$$

$$\Delta U_{12} = 0$$

Along the isobar (2-3):

$$q_{23} = nc_p (T_3 - T_2) = \frac{c_p}{R} (p_3 V_3 - p_2 V_2) = \frac{7}{2} (p_2 V_1 - p_2 V_2)$$

$$w_{23} = -p_2 (V_3 - V_2) = -p_2 (V_1 - V_2)$$

$$\Delta U_{23} = nc_v (T_3 - T_2) = \frac{c_v}{R} (p_3 V_3 - p_2 V_2) = \frac{5}{2} (p_2 V_1 - p_2 V_2)$$

Along the isochore (3-1)

$$q_{31} = nc_v (T_1 - T_3) = \frac{c_v}{R} (p_1 V_1 - p_3 V_3) = \frac{5}{2} (p_1 V_1 - p_2 V_1)$$

$$w_{31} = 0$$

$$\Delta U_{31} = q_{31} = \frac{5}{2} (p_1 V_1 - p_2 V_1)$$

Path	$q$	$w$	$\Delta U$
1-2 (isotherm)	$p_1 V_1 \ln\left(\frac{V_2}{V_1}\right)$ or $p_1 V_1 \ln\left(\frac{p_1}{p_2}\right)$	$-p_1 V_1 \ln\left(\frac{V_2}{V_1}\right)$ or $-p_1 V_1 \ln\left(\frac{p_1}{p_2}\right)$	0
2-3 (isobar)	$\frac{7}{2}(p_2 V_1 - p_2 V_2)$	$-p_2(V_1 - V_2)$	$\frac{5}{2}(p_2 V_1 - p_2 V_2)$
3-1 (isochore)	$\frac{5}{2}(p_1 V_1 - p_2 V_1)$	0	$\frac{5}{2}(p_1 V_1 - p_2 V_1)$

2 pts per correct value. No credit for answers that contain  $p_3$ ,  $V_3$ ,  $T_1$ ,  $T_2$ , or  $T_3$  (because we told you not to!). Half credit for answers that assume a monatomic or non-linear triatomic gas

c) Consider each path separately. The equations that we need are

$$\Delta S_{\text{sys}} = \int \frac{dq_{\text{rev}}}{T} \text{ (definition of change in entropy)}$$

$$\Delta S_{\text{isotherm}} = \frac{q}{T}$$

$$\Delta S_{\text{isobar}} = n c_p \int \frac{dT}{T} = n c_p \ln \frac{T_f}{T_i}$$

$$\Delta S_{\text{isochore}} = n c_v \int \frac{dT}{T} = n c_v \ln \frac{T_f}{T_i}$$

$$c_p = c_v + R \text{ (any ideal gas)}$$

$$c_v = \frac{5}{2} R \text{ (ideal diatomic gas)}$$

$$\Delta S_{\text{surr}} = -\Delta S_{\text{sys}} \text{ (reversible process)}$$

These equations give us

$$\Delta S_{12} = nR \ln\left(\frac{V_2}{V_1}\right)$$

$$\Delta S_{23} = \frac{7}{2} nR \ln\left(\frac{T_3}{T_2}\right) = \frac{7}{2} nR \ln\left(\frac{p_2 V_1}{p_2 V_2}\right) = \frac{7}{2} nR \ln\left(\frac{V_1}{V_2}\right)$$

$$\Delta S_{31} = \frac{5}{2} nR \ln\left(\frac{T_1}{T_3}\right) = \frac{5}{2} nR \ln\left(\frac{p_1 V_1}{p_2 V_1}\right) = \frac{5}{2} nR \ln\left(\frac{p_2 V_2}{p_2 V_1}\right) = \frac{5}{2} nR \ln\left(\frac{V_2}{V_1}\right)$$

Path	$\Delta S_{\text{sys}}$	$\Delta S_{\text{surr}} = -\Delta S_{\text{sys}}$
1-2 (isotherm)	$nR \ln\left(\frac{V_2}{V_1}\right)$	$-nR \ln\left(\frac{V_2}{V_1}\right)$
2-3 (isobar)	$\frac{7}{2} nR \ln\left(\frac{V_1}{V_2}\right)$	$-\frac{7}{2} nR \ln\left(\frac{V_1}{V_2}\right)$
3-1 (isochore)	$\frac{5}{2} nR \ln\left(\frac{V_2}{V_1}\right)$	$-\frac{5}{2} nR \ln\left(\frac{V_2}{V_1}\right)$

(2 pts per correct value. No credit for answers that contain pressure, temp, or  $V_3$ . Half credit for answers that assume a monatomic or non-linear triatomic gas)

d) The overall  $\Delta U_{\text{tot}}$  is (keeping in mind that  $p_1 V_1 = p_2 V_2$ )

$$\Delta U_{TOT} = 0 + \frac{5}{2}(p_2 V_1 - p_2 V_2) + \frac{5}{2}(p_1 V_1 - p_2 V_1)$$

$$\Delta U_{TOT} = 0 + \frac{5}{2}(p_2 V_1 - p_1 V_1) + \frac{5}{2}(p_1 V_1 - p_2 V_1)$$

$$\Delta U_{TOT} = 0$$

(3 pts for showing math leading to  $\Delta U_{TOT}=0$ )

The overall  $\Delta S_{\text{sys,tot}}$  is

$$\Delta S_{\text{sys,tot}} = nR \ln\left(\frac{V_2}{V_1}\right) + \frac{7}{2}nR \ln\left(\frac{V_1}{V_2}\right) + \frac{5}{2}nR \ln\left(\frac{V_2}{V_1}\right)$$

$$\Delta S_{\text{sys,tot}} = nR \ln\left(\frac{V_2}{V_1}\right) - \frac{7}{2}nR \ln\left(\frac{V_2}{V_1}\right) + \frac{5}{2}nR \ln\left(\frac{V_2}{V_1}\right)$$

$$\Delta S_{\text{sys,tot}} = 0$$

(3 pts for showing math leading to  $\Delta S_{\text{sys,tot}}=0$ )

**Problem 2 – Equilibrium of Hydrogen Iodide (20 points)**

a)

$$\Delta G^0 = -RT \ln K_{eq} = -(8.3144721 \text{ J mol}^{-1} \text{ K}^{-1})(300 \text{ K}) \ln [50.5] = -9.78 \times 10^3 \text{ J mol}^{-1}$$

A negative  $\Delta G^0$  implies that the forward reaction is thermodynamically spontaneous.

(1 point for equation, 2 points for numerical answer, 3 points for spontaneous. No credit for a numerical answer with incorrect units or sigfigs)

b)

Let  $x$  represent  $[\text{H}_2]$  and  $[\text{I}_2]$  at equilibrium. Then

$$K_{eq} = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(150 \text{ torr} - 2x)^2}{x^2} = 50.5 \quad (3 \text{ points})$$

We hinted to simplify the calculation by letting  $[\text{HI}]$  remain “constant”, because you don’t get access to Mathematica on this quiz. Our equation reduces to

$$\frac{(150 \text{ torr})^2}{x^2} = 50.5$$

$$x^2 = 446 \text{ torr}^2$$

$$x = 21.1 \text{ torr} = [\text{H}_2] = [\text{I}_2]$$

$$[\text{HI}] = 108 \text{ torr}$$

(1.5 points  $[\text{H}_2]$ , 1.5 points  $[\text{I}_2]$ , 2 points  $[\text{HI}]$ , no credit for incorrect units or sigfigs)

Note: If we solve this equation rigorously, we obtain the quadratic equation (and solution)

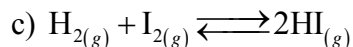
$$93x^2 + (1200 \text{ torr})x - (45000 \text{ torr}^2) = 0$$

$$x = 16.5 \text{ torr} = [\text{H}_2] = [\text{I}_2]$$

$$[\text{HI}] = 117 \text{ torr}$$

(Full credit for solving this quadratic equation rather than approximating that  $[\text{HI}]$  is constant)

The assumption that  $[\text{H}_2]$  and  $[\text{I}_2]$  are much less than  $[\text{HI}]$  is pretty bad. We overestimate  $[\text{H}_2]$  and  $[\text{I}_2]$  by 14%, which can render a kinetics or spectroscopy experiment useless. In real life, just because something is easy doesn’t make it a good thing to do!



By Le Chatelier’s principle, if  $\text{I}_2$  condenses, the reaction will shift towards the reactants to relieve the “stress” put on the system. Therefore,  $[\text{HI}]$  will decrease and  $[\text{H}_2]$  will increase.

(2 points  $[\text{HI}]$  decreases, 2 points  $[\text{H}_2]$  increases, 2 points anything related to Le Chatelier, stress on the system, or  $Q > K_{eq}$ . Full credit for a mathematical argument based on  $K_{eq}$ )

**Problem 3 – Buffering a Frenemy (20 points)**

a)

$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = 1.8 \times 10^{-5} \text{ M}$$

$$\frac{x^2}{1.00 \text{ M} - x} \xrightarrow{\text{weak acid, } x \ll 1.00 \text{ M}} \frac{x^2}{1.00 \text{ M}} = 1.8 \times 10^{-5} \text{ M}$$

$$x = 4.2 \times 10^{-3} \text{ M} = [\text{H}^+]$$

$$\text{pH} = -\log[\text{H}^+] = 2.37$$

(2 pts  $K_a$  expression, 2 pts for math, 2 pts for pH. No credit for incorrect sigfigs)

b) We need a pH of 4.30, so the final  $[\text{H}^+]$  will be  $5.0 \times 10^{-5} \text{ M}$ . Furthermore, the sodium acetate fully dissociate upon being added to the solution. Let's set up a table to keep track of things:

	$[\text{CH}_3\text{COOH}]$	$[\text{H}^+]$	$[\text{CH}_3\text{COO}^-]$
Initial Concentrations	1.00 M	$4.2 \times 10^{-3} \text{ M}$	$4.2 \times 10^{-3} \text{ M}$
Immediately after adding salt	1.00 M	$4.2 \times 10^{-3} \text{ M}$	$(x + 4.2 \times 10^{-3}) \text{ M}$
At new Equilibrium	$(1.00 - 4.15 \times 10^{-3}) \text{ M}$	$5.0 \times 10^{-5} \text{ M}$	$(x + 5.0 \times 10^{-5}) \text{ M}$

$x$  is the amount of acetate anion that is added. The amount of acetic acid only changes by the amount amount of protons consumed by the acetate anion.

(2 pts table or any other logical setup)

The concentrations at our new equilibrium must still satisfy the equilibrium constant. So,

$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{(5.0 \times 10^{-5} \text{ M})(5.0 \times 10^{-5} \text{ M} + x)}{(1.00 \text{ M} - 4.15 \times 10^{-3} \text{ M})} = 1.8 \times 10^{-5} \text{ M}$$

Now we solve for  $x$

$$x = \left( \frac{1.8 \times 10^{-5} - 7.5 \times 10^{-8}}{5.0 \times 10^{-5}} \right) \text{ M} - 5.0 \times 10^{-5} \text{ M} \quad (2 \text{ pts math})$$

$$x = 0.35 \text{ M}$$

Since we are working with 1.00 L of solution, **we would add 0.35 mol of  $\text{CH}_3\text{COONa}$ .**

Note that we have not changed the concentration of acetic acid, it essentially remains at 1.00 M.

(2 pts final answer. No credit for incorrect sigfigs or units)

c) Sodium hydroxide is a strong base, and will completely dissociate into  $\text{Na}^+$  and  $\text{OH}^-$ . One way to approach this problem is to define our starting point as after all of the  $\text{OH}^-$  has reacted with the acetic acid to form water and acetate anion. Again, we make a table to organize our thoughts.

	$[\text{CH}_3\text{COOH}]$	$[\text{H}^+]$	$[\text{CH}_3\text{COO}^-]$
Concs. from part b)	1.00 M	$5.0 \times 10^{-5} \text{ M}$	0.35 M
Immediately after NaOH reacts	0.90 M	$5.0 \times 10^{-5} \text{ M}$	0.45 M
Final equilibrium	$0.90 \text{ M} + x$	$5.0 \times 10^{-5} \text{ M} - x$	$0.45 \text{ M} - x$

(2 pts for table or any logical setup)

Here, we subtract  $x$  from  $[H^+]$  because according to Le Chatelier's principle, we need to "relieve the stress" of having lost acetic acid.

The equilibrium equation is

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = \frac{[H^+](0.45\text{ M} - x)}{(0.90\text{ M} + x)} = 1.8 \times 10^{-5}\text{ M}$$

Because we are working with a buffered solution, the change in  $[H^+]$  should be vastly less than the concentrations of acetic acid and acetate (in other words,  $x \ll 0.45\text{ M}$ ), so we can simplify this expression. (We can check this assumption at the end of the problem)

$$\frac{[H^+](0.45\text{ M})}{(0.90\text{ M})} = 1.8 \times 10^{-5}\text{ M}$$

$$[H^+] = 3.6 \times 10^{-5}\text{ M} \quad (2\text{ pts math})$$

$$\text{pH} = -\log[H^+] = 4.44$$

(2 pts final answer. No credit for incorrect sigfigs)

This answer tells us that  $x = 1.4 \times 10^{-5}\text{ M}$ , so our assumption of  $x \ll 0.45\text{ M}$  was valid.

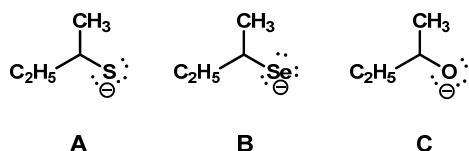
The acceptable range for your solution was  $4.30 \pm 0.30$ , and your frenemy only managed to increase the pH to 4.44. So she failed! You've thwarted her this time, but you might consider getting some new friends.

(2 pts for conclusion that is consistent with calculated pH)

Buffers aren't really meant to prevent acts of sabotage, but I suppose it helped here.

**Problem 4 – Acidity of Organic Molecules (20 points)**

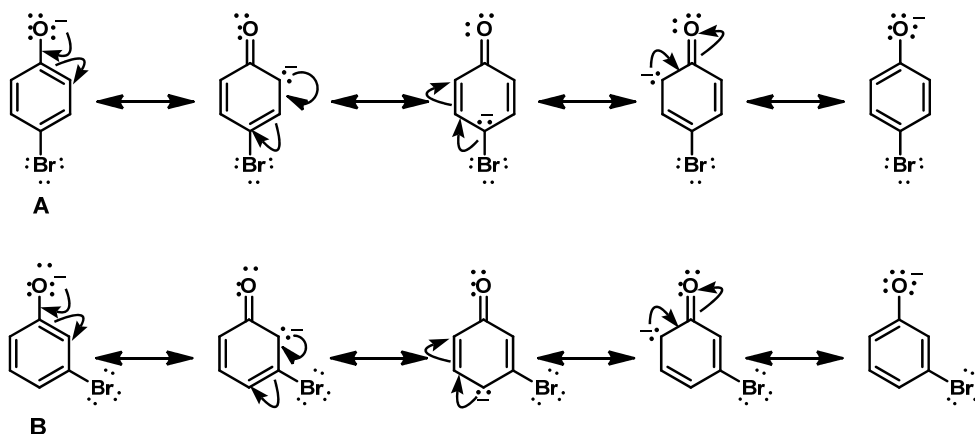
a) Conjugate bases of the listed acids



**C < A < B.** O, S, and Se are in the same column in the periodic table. As we go down a column in the periodic table, the atomic radius increases and as the atomic radius increases, that atom can better accommodate negative charge. Since the atomic radius increases going from O to S to Se, the acidity increases going from C to A to B.

5 pts for conjugate bases (-2 for each incorrect or missing structure, no credit for a structure missing lone pairs or formal charges), 2 pts for correct order, 3 pts for reasonable argument.

b) Conjugate bases of the listed acids



ii) A < B: B is more acidic than A because of a increased inductive effect. Both B and A are more acidic than phenol due to inductive stabilization of the introduced negative charge. However, because inductive effects decrease as the distance from the negative charge increases, B is more acidic than A. Listed below are the pKas of A, B, and 2-bromophenol (from the National Library of Medicine website (<http://toxnet.nlm.nih.gov/>)).

A: pKa: 9.17

B: pKa: 9.03

2-bromophenol: pKa: 8.45

5 pts for conjugate bases (-2 for each incorrect or missing structure, no credit for a structure missing lone pairs or formal charges)

**Due to an error in the grading and original key, we have thrown out the final part of this question (order, reason)  
The quiz is now scored out of 95 points**