

- a) P_4O_{10} b) SO_3 c) CO_2 d) NO_2 **e) all of the above**

Remember the lecture demonstrations where we showed that CO_2 and P_4O_{10} produced an acidic response in universal indicator solutions? You should expect other non-metallic oxides such as SO_3 and NO_2 to behave similarly. Thus, (e) is the best answer.

2. The pH of a solution is best expressed by.....

a) $-\log[\text{H}_3\text{O}^+]$ b) $14 - \log[\text{OH}^-]$ c) $-\log K_w/[\text{OH}^-]$

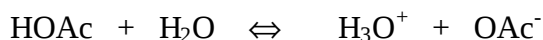
d) $\text{pK} + \log [\text{A}^-]/[\text{HA}]$ **e) all of the above**

If you go through the list of answers, only (b) is INCORRECT (because of the minus sign). Remember that the sum of the pH and the pOH is 14. Therefore correct answers to the question are (a), (c) and (d).

3. You have before you a beaker half-filled with a clear liquid and an apparatus for qualitatively demonstrating conductivity by plunging in a pair of electrodes attached to a light bulb and observing the intensity of the illumination that results by completing the circuit. To begin with, there is no illumination. On adding water the bulb glows, and then glows more strongly, as more water is added. The original liquid is most likely.....

a) pure water **b) pure (glacial) acetic acid**
 c) pure (absolute) ethanol d) vinegar, a dilute acetic acid solution
 d) sea water

If you remember the lecture demonstration, the best answer is (b). If you don't, then work through the other answers: water is nonconducting, and alcohol, being similar, is not conducting; sea water is salt water, and conducting; that leaves us with acetic acid which becomes increasingly conducting when diluted with water, a bronsted base (to acetic acid).



4. Changing the pH of an aqueous solution by a factor of 2 reflects a change in the hydronium ion concentration by a factor of...

a) 2 b) 20 **c) 100** **d) 1000** e) 2000

There is no factor of 2 that will produce answers (a), (b), or (e); but 2 to 4, a factor of 2, gives (c) as an answer as a two pH unit difference is a difference of two orders of magnitude (100) in hydronium ion concentration; and 3 to 6, again a factor of 2, gives a difference of 3 pH units and three orders of magnitude difference (1000) in hydronium ion concentration. So either (c) or (d) is correct.

5. If an 0.20 M solution of a weakly acidic monoprotic acid HX has a pH of 3.0, then the K_a of this acid must be....

a) 6×10^{-1} b) 1×10^{-3} c) 3×10^{-3} d) 2×10^{-4} **e) 5×10^{-6}**

For the reaction $\text{HX} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{X}^-$

$$K(\text{HX}) = [\text{H}_3\text{O}^+][\text{OH}^-]/\text{HX}$$

$$[\text{H}_3\text{O}^+] = [\text{X}^-] = 10^{-3}\text{M}$$

$$= [10^{-3}][10^{-3}]/.2 = 10^{-6}/.2 = 5 \times 10^{-6}$$

And the answer is (e)

6. The equilibrium constant for the autoprotolysis of water as given by the following equation is 1.00×10^{-14} at 25°C : $\text{H}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$

To a close approximation, the pH of a 10^{-10}M solution of HCl is

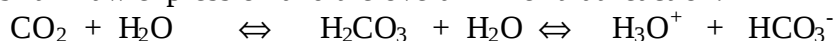
- a) 1 b) 4 c) 7 d) 10 e) 14

The hydronium ion concentration in water itself is 10^{-7}M , three orders of magnitude greater, so the best answer is pH = 7, reflecting the hydronium ion concentration of water.

7. Aqueous carbon dioxide solutions – that's carbonated water, or SELTZER, folks - can be thought of as aqueous solutions of weakly carbonic acid (H_2CO_3). At 25°C , if the concentration of water saturated with carbon dioxide is 0.01 M and if the $K_a(1)$ and $K_a(2)$ values for carbonic acid are respectively 10^{-7} and 10^{-11} , then the pH of the solution must be about....

- a) 3.2 **b) 4.5** c) 5.0 d) 7.0 e) 9.0

This problem is similar to the H_2S MORE problems on the homework. Assume the first dissociation is the only one of significance and go from there. Tough problem but if you make some simplifying assumptions, not so tough. Begin with the assumption that only the first equilibrium need be considered as the second gives very, very little H_3O^+ and find the equilibrium law expression and the overall K for that reaction:

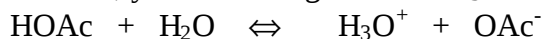


$k_a(\text{CO}_2) = 10^{-7} = [\text{x}][\text{x}]/.01$ where $\text{x} = [\text{H}_3\text{O}^+]$; Finally, algebra gives (b).

8. The K_a for formic acid, a monoprotic acid, is 1.8×10^{-4} . If 100 mL of 1.0M HCl is added (carefully) to 900 mL of a solution prepared by dissolving 0.60 mole of sodium formate (HCOONa) and 0.40 mole of formic acid (HCOOH) in water, then the final pH of the resulting liter of solution must be.....

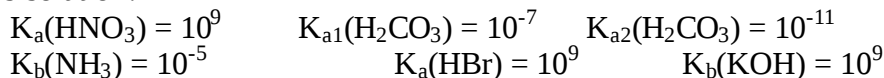
- a) 3.57 b) 3.92 **c) 3.74** **d) equal to the pK_a** **e) both (c) and (d)**

This is a modification of a textbook homework problem from Chapter 8. If you add 100mL of 1 M HCl, you are adding 0.1 mole H_3O^+ which reduces OAc^- by 0.1 mole



and increases HOAc by 0.1 mole, making $\text{HOAc} = \text{OAc}^-$ and pH = pK

9. For each salt below, which set of answers best describes the properties of its aqueous solution?



- | | | |
|-------------------|-------------------------|------------------------|
| KNO_3 | K_2CO_3 | NH_4Br |
| a) neutral | basic | basic |
| b) acidic | acidic | basic |
| c) basic | basic | acidic |
| d) neutral | acidic | basic |
| e) neutral | basic | acidic |

Hydrolysis of KNO_3 leads to a neutral response

Hydrolysis of K_2CO_3 gives a basic response

Hydrolysis of NH_4Br gives an acidic response

10. With respect to the precipitation of sparingly soluble salts, which of the following is/are true?

- a) If no solid phase is present, then the concentrations of the ions in solution bear no relationships to each other.
- b) If the ion product is less than the K_{sp} , then the solid phase cannot exist.
- c) If the ion product equals the K_{sp} , then precipitation occurs.
- d) All of the above are true
- e) Only (a) and (b) are true.**

(c) is wrong because by definition, it is the limit of solubility, or the point BEYOND which precipitation occurs. So (e) is the best answer.

11. If for sparingly soluble calcium phosphate K_{sp} is known to be 1.3×10^{-32} , then the solubility of calcium phosphate in water at 25°C must be about....

- a) 1.1×10^{-16}
- b) 1.5×10^{-11}
- c) 1.6×10^{-7}**
- d) 4.2×10^{-7}
- e) 4.8×10^{-7}

Let x = solubility. $\text{Ca}_3(\text{PO}_4)_2(\text{s}) \rightleftharpoons 3 \text{Ca}^{2+} + 2 \text{PO}_4^{3-}$

$$K_{\text{sp}} = [\text{Ca}^{2+}]^3 [\text{PO}_4^{3-}]^2 = [3x]^3 [2x]^2 = 108x^5 = 1.3 \times 10^{-32}; x = (\text{c}) \text{ above}$$

12. To increase the solubility of sparingly soluble silver chloride in water, add aqueous

- a) silver nitrate
- b) sodium chloride
- c) ammonia**
- d) hydrochloric acid
- e) sodium hydroxide

Common ions limit (decrease) solubility as we demonstrated in class by shifting the equilibrium in favor of the precipitated salt, according to Le Chatelier's principle. That means (a), (b), and (d) are wrong. Sodium hydroxide will precipitate the insoluble oxide (hydroxide of silver). But ammonia forms a soluble complex.

13. 1.000 g of copper (Cu) at 300K and 1.000 g of iron (Fe) at 500K are brought into contact with one another, but isolated from everything else. What is the temperature of the copper when thermal equilibrium is reached?

- a. 392.3K
- b. 398.7K
- c. 401.3K
- d. 407.7K**
- e. 409.3K

This is a direct use of the relation $m_1 \times c_{s,1} \times ?T_1 = -m_2 \times c_{s,2} \times ?T_2$ presented on slide 25 from the first lecture and on p. 445 of your text.

14. A 7.0 kg bowling ball is attached to a collection of pulleys and levers that allows all its downward motion to be used to compress a gas in a piston-and-cylinder arrangement that is our thermodynamic system. What is the work w when the bowling ball falls the 9.6m from the ceiling of 309 Havemeyer Hall to the floor?

- a. 0.45 kJ
- b. 0.51 kJ
- c. 0.66 kJ**
- d. 1.5 kJ
- e. 2.0 kJ

This is exactly analogous to Joule's demonstration of the mechanical equivalent of heat, presented on slides 6 and 7 of lecture 2, and on p. 468 of your text. It is also a much simpler version of problem 89 in Chapter 10 of your text, and the in-class worked problem on slide 1 of lecture 2. w = work done on the gas = - work done by the ball = $-m \times g \times ?h$. Note that since the gas is compressed the work done on the gas has to be positive, which is why none of the multiple choices is negative.

15. When 1.0000 mole of graphite at 298K is burned in oxygen 393.51 kJ of heat is released. When 1.0000 mole of diamond at 298K is burned in oxygen 395.41 kJ of heat is released. From this calculate the enthalpy change associated with the phase change $C(s, \text{diamond}) \rightarrow C(s, \text{graphite})$ at 298K (in kJmol^{-1})

a. **-1.90** b. -0.90 c. -0.19 d. +0.90 e. +1.90

This is a simpler version of problem 33 in Chapter 10 of your text. It is also the subject of problem 35. The ΔH is given on p. 457 of your text, where the enthalpy change associated with the conversion of graphite to diamond is discussed.

16. A gas in a cylinder with a piston starts out at equilibrium with $P = 1.50 \times 10^5 \text{ Pa}$, $V = 2.00 \times 10^{-2} \text{ m}^3$ and $T = 300\text{K}$. Then a constant pressure of $3.50 \times 10^5 \text{ Pa}$ is applied to the piston, compressing the gas to $1.00 \times 10^{-2} \text{ m}^3$. The pressure on the sample is reduced to $1.50 \times 10^5 \text{ Pa}$ and the gas expands against this constant pressure of $1.50 \times 10^5 \text{ Pa}$ from $1.00 \times 10^{-2} \text{ m}^3$ back to a volume of $2.00 \times 10^{-2} \text{ m}^3$ ending at a temperature of 300K. Calculate ΔE for the overall process.

a. -2.00 kJ b. **0.00 kJ** c. +1.50 kJ d. +2.00 kJ e. +3.50 kJ

This is a variation of the PV work calculations in the example done in class on slides 19 and 20 of lecture 2, and the in-class problem presented along with it. There is no way to calculate ΔE here. While you can calculate w , q is not defined. But, you need not do any calculation. Rather, you need only use the fact that E is a state function, and note that P , V , and T are the same at the end of the process as at the beginning to determine that $\Delta E = 0$. Slides 24-26 of lecture 2 explain that P , V , and T uniquely specify the state of a system, that E is a state function, and that thus E cannot change if P , V , and T do not.

17. The thermite reaction is $2\text{Al}(s) + \text{Fe}_2\text{O}_3(s) \rightarrow 2\text{Fe}(s) + \text{Al}_2\text{O}_3(s)$. Calculate the standard enthalpy of this reaction (in kJmol^{-1}):

a. **-852** b. -824 c. -426 d. +426 e. +852

This is problem 40, part a. from Chapter 10 of your text. It requires use of the formula relating ΔH_r to ΔH_f , given on slide 25 of lecture 3 and on p. 458 of your text.

18. Calculate the standard specific enthalpy of combustion (in kJg^{-1}) for $\text{CH}_4(g) + \text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(g)$.

The standard specific enthalpy of combustion is the enthalpy change per unit mass of fuel consumed at the standard state.

a. -35.1 b. **-50.2** c. -54.9 d. -55.7 e. -59.6

This is a simpler version of problem 48 in Chapter 10 of your text. First calculate ΔH_r in the usual way (see slide 25 of lecture 3 or p. 458 of your text) to get the enthalpy change per mole of reaction as written, then divide by the mass of methane (16 g) consumed per mole of reaction.

19. Calculate the standard enthalpy of reaction (in kJmol^{-1}) for $\text{Na}(g) + \text{Cl}(g) \rightarrow \text{NaCl}(s)$

- a. -182 b. -396 c. -426 d. -533 **e. -640**

This is just like problem 83, part b. in Chapter 10 of your text. It just uses the equation for ΔH_r given on slide 25 of lecture 3 and p. 458 of your text.

20. A constant pressure of 7.00 atm is exerted on a gas. The gas is cooled and contracts from an initial volume of 2.00 L to a final volume of 0.500 L. Compute the work done (in units of liter-atmospheres) on the gas during the contraction.

- a. -10.5 L-atm b. -3.5 L-atm c. 0.00 L-atm d. +3.5 L-atm **e. +10.5 L-atm**

This is word-for-word problem 61 in Chapter 10 of the text, just the numbers have been changed. It is a direct use of the equation for PV work given on slide 13 of lecture 2 and p. 466 of your text. It is like the example worked out on slide 20 of lecture 2.

21. When 1100 J of energy are added to a particular water-filled calorimeter its temperature rises from 300.00K to 301.55K. When 0.03999 g of NaOH(s) is dissolved in the water in this calorimeter the temperature rises by 5.50 K. Calculate the amount of heat evolved in the dissolution of this NaOH(s) in the water of the calorimeter.

- a. 201 J b. 301 J c. 710 J **d. 3.90 kJ** e. 4.26 kJ

This is exactly like problem 15 in Chapter 10 of your text, except that here you don't have to work through two different amounts of water as you do in that problem.

22. $2.00 \times 10^{-3} \text{ m}^3$ of a gas is confined at a pressure of $1.01 \times 10^5 \text{ Pa}$ and a temperature of 273K. The confining pressure is reduced to zero and the gas is heated to 373K, causing the gas to expand to a final volume of $3.50 \times 10^{-3} \text{ m}^3$. Determine the work done on the gas during the expansion.

- a. -353 J b. -202 J c. -152 J d. -76 J **e. 0.00 J**

This is exactly problem 63 in Chapter 10 of your text, with just a slight change in wording to make clearer that the expansion takes place against a pressure of zero, and a change to SI units. Work is zero if the external pressure is zero, as I explained in lecture on several occasions and your text states explicitly on p. 466.

23. For the reaction $\text{H}_2(\text{g}) + 2\text{CO}(\text{g}) \rightarrow \text{H}_2\text{O}_2(\text{l}) + 2\text{C}(\text{s})$ $\Delta H_r = 33.3 \text{ kJ mol}^{-1}$. Calculate the enthalpy change when 18.0 g of C(s) is produced in this reaction.

- a. 16.7 J **b. 25.0 J** c. 44.4 J d. 50.0 J e. 99.9 J

This uses what is presented on slide 32 of lecture 3, computing ΔH for reaction consuming or producing a particular amount of a particular reactant or product from a knowledge of ΔH_r per mole of reaction as written.

24. You charge up your cell phone battery using the charger that plugs into an outlet in your house. The charger draws 111 J of energy from your house electrical supply, and puts 92 J of electrical energy in the cell phone battery. Calculate the work done on the battery and the heat transferred to the battery in this charging, assuming that all energy that the charger draws from the house electrical supply goes into the battery.

a. $w=111\text{J}, q=-19\text{J}$ b. $w=111\text{J}, q=0\text{J}$ c. $w=92\text{J}, q=-19$ d. $w=92\text{J}, q=0\text{J}$ **e. $w=92\text{J}, q=19\text{J}$**

This is a simpler version of problem 66 in Chapter 10 of your text. It is an application of the first law, $\Delta E = 111\text{ J} = q + w = q + 92\text{ J}$ so $q = 19\text{ J}$.

25. 100 J of PV work is done on a gas, raising its temperature from 273K to 475K. Then the gas is cooled back down to 273K without any work being done on it. What is q for the overall process?

a. -200 J **b. -100 J** c. 0.00 J d. $+100\text{ J}$ e. -200 J

This is just an application of the first law. Since the final state of the gas is the same as the initial state $\Delta E = 0 = q + w$, and since the work done on the gas is $w = 100\text{ J}$ the q for the process must be -100 J .

Heat Capacities and Specific Heats of Some Materials

Material	$C_p(\text{J K}^{-1} \text{mol}^{-1})$	$c_s(\text{J K}^{-1} \text{g}^{-1})$
Al(s)	27.23	1.009
C(s, graphite)	8.23	0.686
C(s, diamond)	6.57	0.548
CH ₄ (g)	34.92	2.183
CO ₂ (g)	37.12	0.8436
Cu(s)	24.46	0.3849
Fe(s)	25.09	0.4493
Zn(s)	25.39	0.3883
O ₂ (g)	28.91	0.9034
H ₂ (g)	30.70	15.35
H ₂ O(l)	75.38	4.184

Standard Enthalpies of Formation

Material	$\Delta H_f^\circ(298\text{K}), \text{kJ mol}^{-1}$
Al ₂ O ₃ (s)	-1,676
CH ₄ (g)	-75
CO ₂ (g)	-394
Cl(g)	122
Fe ₂ O ₃ (s)	-824
H ₂ O(l)	-286
H ₂ O(g)	-242
H ₂ O ₂ (l)	-188
Na(g)	107
NaCl(s)	-411
NaOH(s)	-426