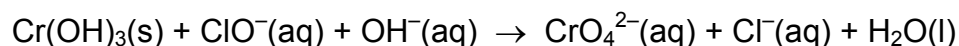


1. Balance the following redox reaction in **basic** solution.

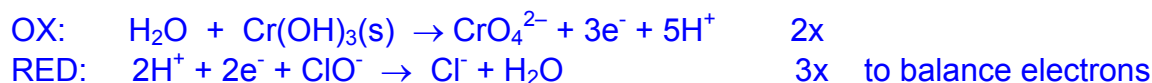


When this has been done correctly, the stoichiometric **coefficients** for $\text{Cr}(\text{OH})_3(\text{s})$, $\text{ClO}^-(\text{aq})$ and $\text{OH}^-(\text{aq})$, in order from **left to right** are:

- A) 2, 3, 4
 B) 2, 4, 6
 C) 1, 2, 3
 D) 3, 4, 5
 E) 1, 1, 4

Cr in $\text{Cr}(\text{OH})_3$ has O.N. = +3; in CrO_4^{2-} has O.N. = +6 ; Cr has a 3 electron oxidation
 Cl in ClO^- has O.N. = +1; in Cl^- has O.N. = -1 ; Cl has a 2 electron reduction

Adding H_2O to reactant and H^+ to product side to balance O and H gives



Add 4 OH^- to BOTH sides to change from acid to base; convert (4H^+ , 4OH^-) to 4 H_2O



ANSWER is A

2. One of the most potent carcinogens (found in air particulate, cigarette smoke and grilled food) is benzo[a]pyrene (molar mass = 252.30 g/mol). Combustion analysis finds that it is 95.21 mass % C and 4.79 mass % H. Which is the **correct molecular formula**?

- A) $C_{20}H_{14}$
B) $C_{19}H_{18}$
C) $C_{18}H_{12}$
D) $C_{20}H_{12}$
E) $C_{22}H_{16}$

Assume 1 mol of benzo[a]pyrene (you can assume any amount – but 1 mol is convenient). Total mass is 252.30 g and 95.1% of that is carbon. Therefore,

$$n_C = 0.9521 \times 252.3 / 12.01 = 20.0$$

$$n_H = 0.0479 \times 252.30 / 1.008 = 12.00$$

Molecular formula is $C_{20}H_{12}$

ANSWER is D

3. In an ice calorimeter, 0.3233 g of Fe are oxidized to Fe^{2+} in an exothermic reaction. As a result, 3.87 g of ice melts, producing water. Calculate how much **heat** (in kJ **per mole of Fe**) is produced. The enthalpy of fusion of ice is $6.012 \text{ kJ} \cdot \text{mol}^{-1}$.

- A) 3.99
B) 223
C) 108
D) 1.29
E) 70.8

$$\Delta H_{\text{fus}}(H_2O) = 6.012 \text{ kJ} \cdot \text{mol}^{-1} \text{ so } 3.87 \text{ g of melted ice requires } 3.87 \times 6.012 / 18 = 1.291 \text{ kJ}$$

$$\text{MW (Fe)} = 55.85 \text{ (P.T.)} \quad n(\text{Fe}) = 0.3233 / 55.85 = 5.789 \times 10^{-3} \text{ mol}$$

$$\text{Heat released per mol Fe: } q = 1.291 / 5.789 \times 10^{-3} = 223 \text{ kJ} \cdot \text{mol}^{-1}$$

ANSWER is B

4. Formic acid, HCOOH , is the monoprotic acid that causes the sting in ant bites. A 0.2361 g sample containing formic acid and an unreactive substance was titrated to the end point by 28.25 mL of a 0.1126 M NaOH solution. What was the **percent purity** (percent **by mass**) of formic acid in the sample?

- A) 41.53 %
 B) 54.80 %
 C) 18.35 %
D) 62.01 %
 E) 6.043 %

$$n(\text{HCOOH}) = 0.02825 \text{ L} \cdot (0.1126 \text{ mol} \cdot \text{L}^{-1}) = 3.181 \times 10^{-3} \text{ mol}$$

$$\text{MW}(\text{HCOOH}) = 12.01 + 2 \cdot (16.00) + 2 \cdot (1.008) = 46.026 \text{ g} \cdot \text{mol}^{-1}$$

$$\text{Mass}(\text{HCOOH}) = 3.181 \times 10^{-3} \text{ mol} \cdot 46.026 \text{ g} \cdot \text{mol}^{-1} = 0.1464 \text{ g}$$

$$\text{Purity (\% by mass)} = 100 \cdot 0.1462 \text{ g} / 0.2361 \text{ g} = 62.01 \%$$

ANSWER is D

5. Calculate the standard enthalpy of formation of **liquid benzene**, C_6H_6 , in kJ mol^{-1} , from its standard enthalpy of combustion which is $-3268 \text{ kJ mol}^{-1}$.
 Data:

$$\Delta H_f^\circ(\text{H}_2\text{O}, \text{l}) = -285.8 \text{ kJ mol}^{-1}$$

$$\Delta H_f^\circ(\text{CO}_2, \text{g}) = -393.5 \text{ kJ mol}^{-1}$$

$$\Delta H_f^\circ(\text{C, diamond}) = 1.90 \text{ kJ mol}^{-1}$$

$$\Delta H_f^\circ(\text{CO, g}) = -110.5 \text{ kJ mol}^{-1}$$

- A) -48
 B) -52
 C) 52
D) 50
 E) -50

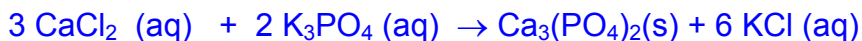
All species (g) if not indicated otherwise		ΔH in kJ mol^{-1}
Combustion:	$\text{C}_6\text{H}_6(\text{l}) + 7.5 \text{ O}_2 \rightarrow 6 \text{ CO}_2 + 3 \text{ H}_2\text{O}(\text{l})$	-3268
Reversed combustion	$6 \text{ CO}_2 + 3 \text{ H}_2\text{O}(\text{l}) \rightarrow \text{C}_6\text{H}_6(\text{l}) + 7.5 \text{ O}_2$	3268
Formation of water(liq)	$3 \times (\text{H}_2 + \frac{1}{2} \text{ O}_2 \rightarrow \text{H}_2\text{O}(\text{l}))$	$3 \cdot (-285.8)$
Formation of CO_2	$6 \times (\text{C}(\text{graphite}) + \text{O}_2 \rightarrow \text{CO}_2)$	$6 \cdot (-393.5)$
TOTAL	$6 \text{ C}(\text{graphite}) + 3 \text{ H}_2 \rightarrow \text{C}_6\text{H}_6(\text{l})$	+49.6

ANSWER is D

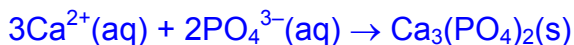
6. If a reaction will occur, identify the correct **net ionic equation** for the reaction of calcium chloride with potassium phosphate, in water:

- A) No net reaction occurs
B) $3\text{Ca}^{2+}(\text{aq}) + 2\text{PO}_4^{3-}(\text{aq}) \rightarrow \text{Ca}_3(\text{PO}_4)_2(\text{s})$
C) $\text{CaCl}_2(\text{aq}) + \text{K}_3\text{PO}_4(\text{aq}) \rightarrow \text{Ca}_3(\text{PO}_4)_2(\text{aq}) + \text{KCl}(\text{aq})$
D) $\text{Ca}^{2+}(\text{aq}) + \text{K}_2\text{PO}_4(\text{aq}) \rightarrow \text{Ca}_3(\text{PO}_4)_2(\text{s}) + 2\text{K}^+(\text{aq})$
E) $\text{K}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{KCl}(\text{s})$

This is a PRECIPITATION reaction since phosphates are insoluble



Net ionic equation is one without SPECTATOR ions



ANSWER is B

7. Which **one** of the following reactions is an oxidation-reduction reaction?

- A) $\text{KCl}(\text{aq}) + \text{AgNO}_3(\text{aq}) \rightarrow \text{AgCl}(\text{s}) + \text{KNO}_3(\text{aq})$
B) $\text{SrCO}_3(\text{s}) \rightarrow \text{SrO}(\text{s}) + \text{CO}_2(\text{g})$
C) $\text{NaOCl}(\text{aq}) + \text{CO}(\text{g}) \rightarrow \text{NaCl}(\text{aq}) + \text{CO}_2(\text{g})$
D) $\text{NaNH}_2(\text{s}) + 2 \text{HBr}(\text{aq}) \rightarrow \text{NaBr}(\text{aq}) + \text{NH}_4\text{Br}(\text{aq})$
E) $\text{SiCl}_4(\text{l}) + 2 \text{H}_2\text{O}(\text{l}) \rightarrow 4 \text{HCl}(\text{aq}) + \text{SiO}_2(\text{s})$

(A) is a precipitation reaction

(B) is a decomposition reaction

(C) is a REDOX reaction

Cl changes O.N. from +1 to -1; C changes O.N. from -2 to -4

(D) is an acid base reaction

(E) is an acid base reaction

ANSWER is C

All of these ions have the electron configuration of argon – since they all have 18 electrons. The only difference is the nuclear charge. Larger nuclear charge produces a smaller ionic radius – the electrons are pulled in more by a larger nuclear charge. Ordering the ions according to decreasing nuclear charge gives the order according to increasing ionic radius:



10. Which **one** of the following is **not** a valid set of quantum numbers, (n, ℓ, m_ℓ) , for an orbital of the hydrogen atom?

- A) 2, 0, 0
 B) 1, 0, 0
 C) 3, 2, -1
 D) 2, 1, 0
 E) 2, 2, 1

Valid quantum numbers for hydrogen are restricted by $n = 1, 2, 3, \dots$, $\ell = 0, 1, \dots, n - 1$ and $-\ell \leq m_\ell \leq \ell$.

2, 2, 1 violates the restriction on the ℓ quantum number. For $n = 2$, there is only $\ell = 0$ and 1.

11. Calculate the **longest wavelength (in μm)** of light **emitted** by an excited hydrogen atom in which the electron occupies the energy level $n = 6$. Note that $1 \mu\text{m} = 10^{-6} \text{ m}$.

- A) 3.28
 B) 93.7
 C) 2.28
 D) 1.00
 E) 7.46

The longest wavelength corresponds to the smallest frequency which corresponds to the smallest energy difference. Since the electron initially occupies the $n = 6$ energy level, and we are considering emission lines, the final energy level must be $n = 5$.

Therefore,

$$h\nu = E_6 - E_5 = -R_H \left(1/6^2 - 1/5^2 \right) = 2.18 \times 10^{-18} \text{ J} \times (1/5^2 - 1/6^2) \\ = 2.66_4 \times 10^{-20} \text{ J}$$

$$\text{So, } \lambda = c / \nu = h c / \nu$$

$$= 6.626 \times 10^{-34} \text{ J s} \times 2.998 \times 10^8 \text{ m s}^{-1} / 2.664 \times 10^{-20} \text{ J}$$

$$= 7.46 \times 10^{-6} \text{ m} = 7.46 \text{ } \mu\text{m}$$

12. Determine the **standard enthalpy of formation (in kJ mol⁻¹)** of solid calcium chloride from the following data (all in kJ mol⁻¹):

$$\Delta H_f^\circ[\text{Ca(g)}] = 178$$

$$\text{First ionization energy of Ca(g)} = 590$$

$$\text{Second ionization energy of Ca(g)} = 1150$$

$$\Delta H_f^\circ[\text{Cl(g)}] = 122$$

$$\text{Electron affinity of Cl(g)} = -349$$

$$\text{Lattice enthalpy of CaCl}_2\text{(s)} = -2260$$

- A) -2126
B) -1418
C) -1906
D) +610
E) -796

Here we have all the steps of a Born-Haber cycle – these steps take elements in their standard states and produce an ionic solid. The net change in enthalpy of all the steps equals the enthalpy of formation of the ionic solid.

Formation reaction of CaCl₂(s):



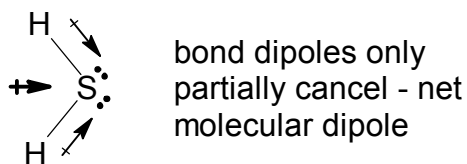
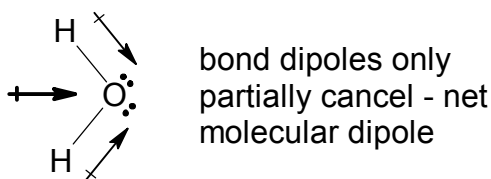
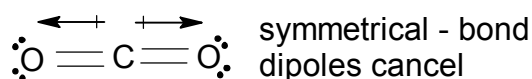
is equivalent to

Ca(s) → Ca(g)	$\Delta H_f^\circ[\text{Ca(g)}]$	178
Ca(g) → Ca ⁺ (g)	$IE_1(\text{Ca})$	590
Ca ⁺ (g) → Ca ²⁺ (g)	$IE_2(\text{Ca})$	1150
Cl ₂ (g) → 2 Cl(g)	$2 \Delta H_f^\circ[\text{Cl(g)}]$	2 × 122
2 Cl(g) → 2 Cl ⁻ (g)	$2 EA_1(\text{Cl})$	2 × (-349)
Ca ²⁺ (g) + 2 Cl ⁻ (g) → CaCl ₂ (s)	$\Delta H_{\text{latt}}^\circ[\text{CaCl}_2\text{(s)}]$	-2260
-----	-----	-----
Ca(s) + Cl ₂ (g) → CaCl ₂ (s)	$\Delta H_f^\circ[\text{CaCl}_2\text{(s)}]$	178+590+1150+244-698-2260 = -796

13. Identify the correct order of **decreasing** molecular dipole moment among the following.

- A) $\text{CO}_2 > \text{H}_2\text{O} > \text{H}_2\text{S}$
- B) $\text{H}_2\text{O} > \text{CO}_2 > \text{H}_2\text{S}$
- C) $\text{H}_2\text{S} > \text{H}_2\text{O} > \text{CO}_2$
- D) $\text{H}_2\text{S} > \text{CO}_2 > \text{H}_2\text{O}$
- E) $\text{H}_2\text{O} > \text{H}_2\text{S} > \text{CO}_2$

Draw the Lewis structures and insert bond dipoles for bonds between atoms with different electronegativities. Larger bond dipoles result from larger differences in electronegativity. Vector addition of bond dipoles produces the net molecular dipole. Molecular symmetry can result in bond dipoles canceling and no molecular dipole – a nonpolar molecule.

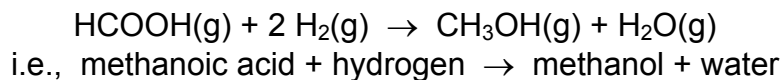


H_2O and H_2S have the same shape. H_2O has the larger molecular dipole because its bond dipoles are larger – since the electronegativity difference is larger for O-H bonds than S-H bonds. CO_2 has no net molecular dipole because of its symmetry – the bond dipoles cancel. Therefore,



is the order according to decreasing molecular dipole.

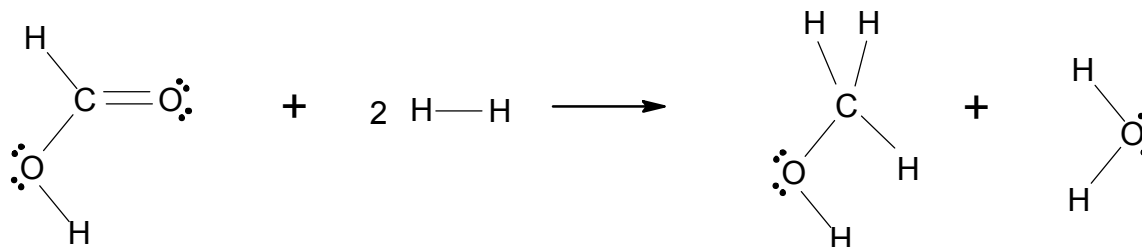
14. Estimate the **enthalpy change** (in kJ per mole of **methanol** produced) of the following gas-phase reaction. (Hint: write the Lewis structures of the molecules before using the given bond enthalpies.)



Bond enthalpies (kJ mol⁻¹): C-C 347; C-O 360; C=O 736; C-H 413;
O-H 464; H-H 436

- A) -172
B) -146
 C) +172
 D) +83
 E) -83

Draw the structures:



The enthalpy of reaction is the sum of the reactant bond enthalpies minus the sum of the product bond enthalpies:

$$\Delta H =$$

$$D(\text{C-H}) + D(\text{C-O}) + D(\text{C=O}) + D(\text{O-H}) + 2 D(\text{H-H}) - [3 D(\text{C-H}) + D(\text{C-O}) + 3 D(\text{O-H})]$$

$$= 413 + 360 + 736 + 464 + 2 \times 436 - [3 \times 413 + 360 + 3 \times 464]$$

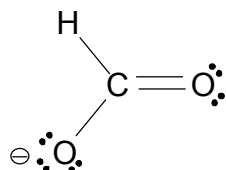
$$= -2 \times 413 + 736 - 2 \times 464 + 2 \times 436$$

$$= -146 \text{ kJ mol}^{-1}$$

15. What is the **shape** of the methanoate anion, HCO_2^- (carbon is the central atom, and both oxygen atoms are terminal)?

- A) T-shaped
B) trigonal planar
C) linear
D) tetrahedral
E) trigonal pyramidal

Methanoate Lewis structure:



Methanoate is AX_3 and therefore trigonal planar.

16. At 125°C , $K_P = 0.25$ for the decomposition of sodium hydrogen carbonate,



If 10.0 g of $\text{NaHCO}_3(\text{s})$ are added to a 1.00 L flask which is then heated to 125°C , what is the **partial pressure of CO_2** (in atm) in the flask when the reaction comes to equilibrium?

- A) 0.75
B) 1.25
C) 0.25
D) 1.0
E) 0.50

Since the activity of pure solids is 1, the equilibrium constant expression is

$K_P = P(\text{CO}_2) \cdot P(\text{H}_2\text{O}) = 0.25 = x^2$ where x is the partial pressure of CO_2 (or H_2O) at equilibrium. Thus $x = (0.25)^{1/2} = 0.50$

ANSWER is E

17. A vessel is filled with $\text{N}_2\text{O}_4(\text{g})$ to an initial pressure of 3.01 atm. Some of this gas decomposes into $\text{NO}_2(\text{g})$. At equilibrium, the partial pressure of $\text{N}_2\text{O}_4(\text{g})$ is found to be 2.71 atm. What is the value of the **equilibrium constant** for the decomposition of $\text{N}_2\text{O}_4(\text{g})$ into $\text{NO}_2(\text{g})$, at the temperature of this experiment?

- A) 1.73
 B) 1.42
 C) 3.11
D) 0.133
 E) 0.233

	N_2O_4	\rightleftharpoons	2NO_2
Initial	3.01		0
Change	-x		2x
Equilibrium	3.01 - x = 2.71		2x

$$K_P = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}}$$

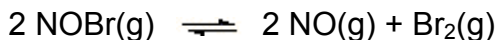
Therefore,

$$x = 3.01 - 2.71 = 0.30 \text{ atm}$$

$$\text{Thus } K_P = (2x)^2 / (3.01 - x) = (2 \cdot 0.3)^2 / 2.71 = 0.133$$

ANSWER is D

18. Pure $\text{NOBr}(\text{g})$ is introduced in an evacuated container. It dissociates according to the following equilibrium:



When equilibrium is established at 25°C , NOBr is 34% dissociated and the total equilibrium pressure P is 0.25 atm. What was the **initial partial pressure** of NOBr (in atm)?

- A) 0.51
 B) 0.073
C) 0.21
 D) 0.39
 E) 0.068

	$2 \text{NOBr}(\text{g})$	\rightleftharpoons	$2 \text{NO}(\text{g})$	$+$	$\text{Br}_2(\text{g})$
Initial	y		0		0
Change	y-x		2x		x
Equilibrium	0.66y		2x		x

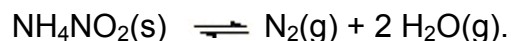
and $2x = 0.34y$ & $x = 0.17y$

$$P_{\text{TOT}} = 0.25 = P_{\text{NO}} + P_{\text{Br}_2} + P_{\text{NOBr}} = (0.34 + 0.17 + 0.66)y$$

$$\rightarrow y = 0.25 / 1.17 = 0.21 \text{ atm}$$

ANSWER is C

19. Solid ammonium nitrite is added to an initially evacuated container. It decomposes according to the chemical equilibrium,



Which of the following statements are **FALSE** regarding this equilibrium?

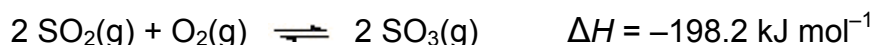
- A) Reducing the volume of the container increases the amount of $\text{NH}_4\text{NO}_2(\text{s})$.
- B) Adding more $\text{NH}_4\text{NO}_2(\text{s})$ to the container does not affect the partial pressure of $\text{N}_2(\text{g})$.
- C) Removing water (via a desiccant - a material that absorbs water) does not affect the amount of $\text{NH}_4\text{NO}_2(\text{s})$.**
- D) The partial pressure of water in the container is twice that of nitrogen.
- E) Pumping additional $\text{N}_2(\text{g})$ into the container increases the amount of solid ammonium nitrite.

$$K_P = P_{\text{N}_2} * P_{\text{H}_2\text{O}}^2$$

- A) reducing volume – reaction will shift to LEFT – statement is TRUE
- B) adding $\text{NH}_4\text{NO}_2(\text{s})$ does not affect position of equilibrium – statement is TRUE
- C) removing $\text{H}_2\text{O}(\text{g})$ - reaction will shift to RIGHT - statement is FALSE**
- D) matches the stoichiometry – statement is TRUE
- E) adding $\text{N}_2(\text{g})$ – reaction will shift to LEFT – statement is TRUE

ANSWER is C

20. Consider the following equilibrium in a container with fixed volume:



Which of the following changes will **NOT** increase the amount of $\text{SO}_2(\text{g})$?

- A) An inert gas is added to increase the total pressure.**
- B) O_2 is removed.
- C) The temperature is increased.
- D) SO_3 is added.
- E) The volume is increased.

$$K_P = \frac{P_{\text{SO}_3}^2}{P_{\text{SO}_2}^2 P_{\text{O}_2}}$$

- A) An inert gas does not affect the partial pressures of reactants or product. This does NOT increase the amount of SO_2 .**

B) Removing O_2 (a reactant) shifts the equilibrium toward reactants. This increases the amount of SO_2 .

C) Le Chatelier's principle tells us that increasing temperature favors the endothermic direction. The forward reaction is exothermic. Therefore, increasing temperature shifts the equilibrium toward reactants – i.e., more SO_2 is formed.

D) Adding SO_3 (a product) shifts the equilibrium toward reactants – i.e., more SO_2 is formed.

E) Increasing the volume decreases the partial pressure of all three gases by the same factor. However, since there are three partial pressures in the denominator of Q (the reaction quotient), Q increases. This shifts the equilibrium toward reactants – i.e., more SO_2 is formed.

21. For the reaction, $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$, the equilibrium constant at $112^\circ C$ is $K_P = 0.220$. For a mixture of $CaCO_3(s)$, $CaO(s)$ and 0.50 atm partial pressure $CO_2(g)$, at $112^\circ C$, which **one** of the following statements is **TRUE**?

- A) $Q > K$, the reaction will proceed to the right.
B) $Q < K$, the reaction will proceed to the left.
C) $Q < K$, the reaction will proceed to the right.
D) $Q = K$, the system is at equilibrium.
E) $Q > K$, the reaction will proceed to the left.

Since the activities of $CaCO_3(s)$ and $CaO(s)$ are one, only the partial pressure of $CO_2(g)$ appears in the reaction quotient:

$$Q_P = P_{CO_2}$$

Thus, a CO_2 partial pressure of 0.50 atm, at $112^\circ C$, corresponds to
 $Q = 0.50 > K = 0.220$.

When $Q > K$, there is net reverse reaction – i.e., the reaction proceeds to the left.

22. PCl_5 (41.6 g) is placed in a 1.00 L vessel and decomposed at $300^\circ C$ ($K_P = 2.455$) to form PCl_3 and Cl_2 . At this temperature, all compounds are in the gas phase. At equilibrium, what is the **partial pressure of PCl_3** (in atm)?

- A) 2.07
B) 4.13
C) 4.67
D) 3.73
E) 0.593

Name: _____

Student number: _____

The initial amount of PCl_5 is

$$n = 41.6 \text{ g} / 208.2 \text{ g mol}^{-1} = 0.199_8 \text{ mol}$$

The initial partial pressure of PCl_5 , at 300°C , is

$$P = n R T / V = 0.199_8 \text{ mol} \times 0.08206 \text{ L atm K}^{-1}\text{mol}^{-1} \times 573.15 \text{ K} / 1.00 \text{ L} = 9.39_7 \text{ atm}$$

	$\text{PCl}_5(\text{g})$	\rightleftharpoons	$\text{PCl}_3(\text{g})$	+	$\text{Cl}_2(\text{g})$
Initial	9.39 ₇		0		0
Change	-x		x		x
Equilibrium	9.39 ₇ - x		x		x

$$K_P = \frac{P_{\text{PCl}_3} P_{\text{Cl}_2}}{P_{\text{PCl}_5}} = \frac{x^2}{9.39_7 - x} = 2.455$$

Therefore,

$$x^2 + 2.455x - 2.455 \times 9.39_7 = 0$$

or

$$x^2 + 2.455x - 23.0_7 = 0$$

which has solutions,

$$x = \frac{-2.455 \pm \sqrt{2.455^2 + 4 \times 23.0_7}}{2}$$

$$= 3.73 \quad \text{choose + sign (otherwise } x < 0)$$

The negative x solution is unphysical – it gives negative partial pressures of the products. Therefore,

$x = 3.73$ = partial pressure of PCl_3 at equilibrium.

23. In which of the following processes does the **entropy of the system decrease**?

- (i) $\text{CH}_4(\text{g}) + 2 \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l})$
- (ii) $\text{B}_2\text{O}_3(\text{s}) + 3 \text{H}_2\text{O}(\text{g}) \rightarrow \text{B}_2\text{H}_6(\text{g}) + 3 \text{O}_2(\text{g})$
- (iii) $\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$
- (iv) $\text{I}_2(\text{s}) \rightarrow \text{I}_2(\text{g})$
- (v) $\text{Li}^+(\text{g}) + \text{F}^-(\text{g}) \rightarrow \text{LiF}(\text{s})$

- A) none
- B) iii, v
- C) all
- D) i, iii, v**
- E) ii, iv

- (i) fewer # moles of gaseous reactants than products → **entropy will DECREASE**
- (ii) greater # moles of gaseous products than reactants → **entropy will INCREASE**
- (iii) fewer # moles of gaseous reactants than products → **entropy will DECREASE**
- (iv) greater # moles of gaseous products than reactants → **entropy will INCREASE**
- (v) fewer # moles of gaseous reactants than products → **entropy will DECREASE**

ANSWER is D

24. When $\text{NH}_3(\text{g})$ reacts spontaneously with $\text{HCl}(\text{g})$, solid NH_4Cl is formed. Which **one** of the following correctly describes the changes in ΔG , ΔH and ΔS ?

- A) $\Delta G > 0$, $\Delta H < 0$, $\Delta S < 0$
- B) $\Delta G < 0$, $\Delta H > 0$, $\Delta S > 0$
- C) $\Delta G > 0$, $\Delta H > 0$, $\Delta S > 0$
- D) $\Delta G < 0$, $\Delta H > 0$, $\Delta S < 0$
- E) $\Delta G < 0$, $\Delta H < 0$, $\Delta S < 0$**



Process is spontaneous → $\Delta G < 0$
 reduced # moles of gas → $\Delta S < 0$

and $\Delta G = \Delta H - T\Delta S$

$\Delta S < 0$ so $-T\Delta S > 0$, thus the reaction can only be spontaneous if $\Delta H < 0$

ANSWER is E

25. The reaction $2 \text{H}_2 (\text{g}) + \text{O}_2 (\text{g}) \rightarrow 2 \text{H}_2\text{O} (\text{g})$ is spontaneous **except** at very high temperature. Which of the following statements is/are **TRUE** for this reaction?

- (i) $\Delta H < 0$
- (ii) $\Delta S < 0$
- (iii) $\text{H}_2 (\text{g})$, $\text{O}_2 (\text{g})$ and $\text{H}_2\text{O} (\text{g})$, all at 1 atm partial pressure, are in equilibrium at very high temperature.
- (iv) $\Delta G < 0$ except at very high temperature.

- A) ii, iv
- B) i, ii
- C) ii, iii
- D) i, ii, iii, iv**
- E) i, iii, iv

(i) since the reaction is spontaneous ($\Delta G < 0$), and $\Delta S < 0$ (fewer gas molecules as products) ΔH must be negative – **the statement is true**

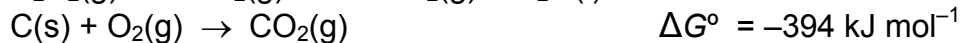
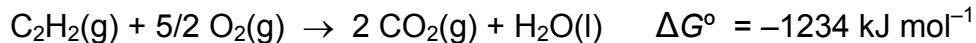
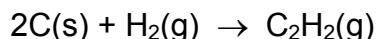
(ii) $\Delta S < 0$ (fewer gas molecules as products) – **the statement is true**

(iii) At some temperature the reverse reaction becomes favorable (see iv). At the switch point, $\text{H}_2 (\text{g})$, $\text{O}_2 (\text{g})$ and $\text{H}_2\text{O} (\text{g})$, all at 1 atm partial pressure will be in equilibrium – **the statement is true**

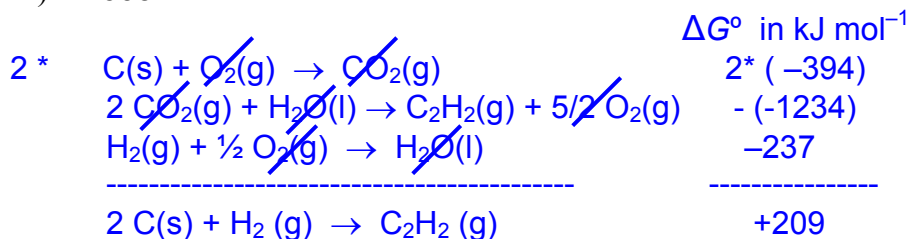
(iv) At some T, $-\Delta S > \Delta H$, and since $-\Delta S$ is +ve, ΔG will become positive – **the statement is true**

ANSWER is D

26. Given the following data, calculate ΔG° (in kJ per mole of $C_2H_2(g)$ produced) for the reaction:



- A) -603
B) +209
 C) +366
 D) -1865
 E) +603



ANSWER is B

27. Calculate the **boiling point** temperature (in °C) of bromine given the following data:

$$\Delta H_f^\circ[\text{Br}_2(g)] = 30.907 \text{ kJ mol}^{-1}$$

$$S^\circ[\text{Br}_2(l)] = 152.2 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$S^\circ[\text{Br}_2(g)] = 245.463 \text{ J K}^{-1} \text{ mol}^{-1}$$

- A) 18
 B) 276
 C) 3
D) 58
 E) 126

At the liquid – gas phase equilibrium, $\Delta G = 0 \rightarrow \Delta H = T\Delta S$

$$T = \Delta H / \Delta S = 30.907 \text{ kJ.mol}^{-1} \cdot 10^3 \text{ J.kJ}^{-1} / (245.46 - 152.2) \text{ J} = 331.4 \text{ K} \rightarrow 58.2^\circ\text{C}$$

ANSWER is D

28. In the process where 1.00 mole of white tin is converted to 1.00 mole of gray tin at 25°C the change in entropy is -7.5 J K^{-1} . Which **one** statement is **TRUE** ?

- A) Gray tin has a higher molar entropy than white tin.
- B) Gray tin is more "ordered" than white tin.**
- C) White tin is more "ordered" than gray tin.
- D) From entropy considerations alone the reaction will be spontaneous.
- E) Gray tin has an entropy of -7.5 J K^{-1} .



- A) gray Sn has less disorder \rightarrow LOWER molar entropy – statement is FALSE
- B) gray Sn has less disorder \rightarrow more ordered – statement is TRUE**
- C) white tin has more disorder \rightarrow less ordered – statement is FALSE
- D) Without ΔH it is not possible to know spontaneous direction – statement is FALSE
- E) -7.5 J K^{-1} is a CHANGE in entropy, not the entropy of gray tin – statement is FALSE

ANSWER is B

29. Which of the following statements is(are) **FALSE**?

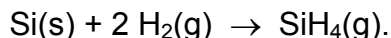
- (i) All spontaneous processes increase the total entropy of the universe.
- (ii) $\Delta G_{\text{sys}} < 0$ for all spontaneous processes.
- (iii) The normal boiling point of a liquid is given by $\Delta H_{\text{vaporization}} / \Delta S_{\text{vaporization}}$.
- (iv) At a given temperature, a reaction proceeds spontaneously in the forward direction if its reaction quotient is larger than its equilibrium constant.

- A) iv**
- B) i
- C) iii, iv
- D) i, ii
- E) ii, iii

- (i) Second law states: $\Delta S_{\text{universe}} > 0$ for all spontaneous processes \rightarrow TRUE
- (ii) $\Delta G_{\text{sys}} < 0$ for all spontaneous processes \rightarrow statement is TRUE**
- (iii) At normal BP $\Delta G = 0$ and $\Delta H_{\text{vap}} = T_{\text{vap}} \Delta S_{\text{vap}} \rightarrow T_{\text{vap}} = \Delta H_{\text{vap}} / \Delta S_{\text{vap}} \rightarrow$ TRUE
- (iv) If $Q > K$ reaction proceeds towards products \rightarrow statement is FALSE**

ANSWER is A

30. Consider the reaction



Use the data below to identify the **TRUE** statement(s).

- (i) $\Delta S^\circ > 0$ for the forward reaction.
- (ii) The reverse reaction is spontaneous at all temperatures.
- (iii) If $P(\text{H}_2) = 100$ atm at equilibrium at 25 °C, then $P(\text{SiH}_4) = 1.10 \times 10^{-6}$ atm.
- (iv) If $P(\text{H}_2) = 100$ atm at equilibrium at 25 °C, then $P(\text{SiH}_4) = 1.10 \times 10^{-4}$ atm.

Data:

$$\begin{aligned}\Delta H_f^\circ(\text{SiH}_4, \text{g}) &= 34.3 \text{ kJ mol}^{-1} \\ S^\circ(\text{H}_2, \text{g}) &= 130.68 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

$$\begin{aligned}S^\circ(\text{SiH}_4, \text{g}) &= 204.62 \text{ J K}^{-1} \text{ mol}^{-1} \\ S^\circ(\text{Si, s}) &= 18.83 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

- A) ii, iv
- B) i, ii
- C) iii
- D) ii, iii**
- E) i

$$\Delta S = S(\text{SiH}_4) - 2 S(\text{H}_2) - S(\text{Si}) = 204.62 - 2 * 130.68 - 18.83 = -75.57 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta G^\circ = \Delta H_f^\circ(\text{SiH}_4, \text{g}) - T \Delta S = 34.2 \text{ kJ} - 298 * (-75.57) \text{ J} * 0.001 \text{ kJ.J}^{-1} = +56.72 \text{ kJ.mol}^{-1}$$

$$\Delta G^\circ = -RT \ln K \rightarrow K = \exp (-56720 \text{ J.mol}^{-1} / 8.31 \text{ J.K.mol}^{-1} * 298) = 1.10 \times 10^{-10}$$

$$\begin{aligned}\text{at } P(\text{H}_2) &= 100 \text{ atm, and equilibrium, } K = 1.10 \times 10^{-10} = P(\text{SiH}_4) / P(\text{H}_2)^2 \\ \rightarrow P(\text{SiH}_4) &= K * P(\text{H}_2)^2 = 1.10 \times 10^{-10} * 100^2 = 1.10 \times 10^{-6}\end{aligned}$$

(i) $\Delta S^\circ < 0$ - \rightarrow statement is FALSE

(ii) for the reverse reaction, ΔH is favorable (exothermic) and ΔS is favorable (+ve) \rightarrow the reverse reaction is favorable at all temperatures \rightarrow statement is **TRUE**

(iii) $P(\text{SiH}_4) = 1.10 \times 10^{-6}$ atm \rightarrow statement is **TRUE**

(iv) statement is FALSE

ANSWER is D

Name: _____

Student number: _____

- Some general data are provided on this page.
- A Periodic Table with atomic weights is provided on the next page.

$$R = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} = 0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}$$

$$c = 2.9979 \times 10^8 \text{ m s}^{-1}$$

$$m_e = 9.10 \times 10^{-31} \text{ kg}$$

$$\text{Specific heat of H}_2\text{O(s)} = 2.03 \text{ J / g} \cdot ^\circ\text{C}$$

$$\text{Specific heat of H}_2\text{O(l)} = 4.18 \text{ J / g} \cdot ^\circ\text{C}$$

$$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$$

$$h = 6.6256 \times 10^{-34} \text{ Js}$$

$$\text{density(H}_2\text{O, l)} = 1.00 \text{ g/mL}$$

$$\Delta H_{\text{fus}}^\circ[\text{H}_2\text{O}] = 6.01 \text{ kJ mol}^{-1}$$

$$\Delta H_{\text{vap}}^\circ[\text{H}_2\text{O}] = 44.0 \text{ kJ mol}^{-1}$$

$$1 \text{ atm} = 101.325 \text{ kPa} = 760 \text{ mm Hg}$$

$$1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2} = 1 \text{ kPa L} = 1 \text{ Pa m}^3$$

$$1 \text{ cm}^3 = 1 \text{ mL}$$

$$1 \text{ Hz} = 1 \text{ cycle/s}$$

$$0^\circ\text{C} = 273.15 \text{ K}$$

$$1 \text{ m} = 10^9 \text{ nm} = 10^{10} \text{ \AA}$$

$$1 \text{ g} = 10^3 \text{ mg}$$

De Broglie wavelength:

$$\lambda = h / mv = h / p$$

Hydrogen atom energy levels:

$$E_n = -R_H / n^2 = -2.178 \times 10^{-18} \text{ J} / n^2$$

Gibbs free energy of reaction: $\Delta G = \Delta G^\circ + RT \ln Q$

$$\text{Entropy change: } \Delta S = \frac{q_{\text{rev}}}{T}$$

Solubility Guidelines for Common Ionic Solids**TABLE 5.1 Solubility Guidelines for Common Ionic Solids**

Follow the lower-numbered guideline when two guidelines are in conflict. This leads to the correct prediction in most cases.

1. Salts of group 1 cations (with some exceptions for Li^+) and the NH_4^+ cation are soluble.
2. Nitrates, acetates, and perchlorates are soluble.
3. Salts of silver, lead, and mercury(I) are insoluble.
4. Chlorides, bromides, and iodides are soluble.
5. Carbonates, phosphates, sulfides, oxides, and hydroxides are insoluble (sulfides of group 2 cations and hydroxides of Ca^{2+} , Sr^{2+} , and Ba^{2+} are slightly soluble).
6. Sulfates are soluble except for those of calcium, strontium, and barium.

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Student number: _____

PERIODIC TABLE OF THE ELEMENTS

I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	13	14	15	16	17	18
1 H 1.0079	2 He 4.0026	3 Li 6.941	4 Be 9.0122	5 B 10.811	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.180	11 Na 22.990	12 Mg 24.305	13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.066	17 Cl 35.453	18 Ar 39.948
19 K 39.098	20 Ca 40.078	21 Sc 44.956	22 Ti 47.88	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.847	27 Co 58.933	28 Ni 58.69	29 Cu 63.546	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.94	43 Tc [98]	44 Ru 101.07	45 Rh 102.91	46 Pd 105.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.75	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57 *La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm [145]	62 Sm 150.36	63 Eu 151.97	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97	72 Hf 178.49
87 Fr [223]	88 Ra 226.03	89 **Ac 227.03	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	94 Pu [244]	95 Am [243]	96 Cm [247]	97 Bk [247]	98 Cf [251]	99 Es [252]	100 Fm [257]	101 Md [258]	102 No [259]	103 Lr [262]	104 Ta 180.95

Atomic weights are based on ¹²C = 12 and conform to the 1987 IUPAC report values rounded to 5 significant digits. Numbers in [] indicate the most stable isotope.

58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm [145]	62 Sm 150.36	63 Eu 151.97	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
* Lanthanides													

90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	94 Pu [244]	95 Am [243]	96 Cm [247]	97 Bk [247]	98 Cf [251]	99 Es [252]	100 Fm [257]	101 Md [258]	102 No [259]	103 Lr [262]
** Actinides													