### Solubility Of Ionic Compounds At SATP

			Anions						
		Cl <sup>-</sup> , Br <sup>-</sup> , I <sup>-</sup>	S-2	OH.	SO <sub>4</sub> <sup>2</sup> -	CO <sub>3</sub> <sup>2-</sup> , PO <sub>4</sub> <sup>3-</sup>	$C_2H_3O_2$	NO <sub>3</sub> -	
7.0	High solubility (aq)	most	Group 1, Group 2,		most	Group 1,	most	all	
ons	≥0.1 mol/L		$NH_4^{+1}$	Sr <sup>2+</sup> , Ba <sup>2+</sup> , Tl <sup>+</sup>		$NH_4^{+1}$			
ati	Low Solubility (s)	Ag+, Pb <sup>2+,</sup> Tl+,	most	most	Ag+, Pb <sup>2+</sup> , Ca <sup>2+</sup> ,	most	Ag <sup>+</sup>	none	
Ü	<0.1 mol/L	Hg <sub>2</sub> <sup>2+</sup> , Cu <sup>+</sup>			Ba <sup>2+</sup> , Sr <sup>2+</sup> , Ra <sup>2+</sup>				

### **Bond Energies at SATP**

Bond	kJ/mol	Bond	kJ/mol	Bond	kJ/mol	Bond	kJ/mol	Bond	kJ/mol	Bond	kJ/mol
Н-Н	432	C-N	305	N-H	391	F-F	154	C=C	614	N=O	607
H-F	565	C-O	358	N-N	160	Cl-Cl	239	C≡C	839	N=N	418
H-Cl	427	C-F	485	N-O	201	Br-Br	193	O=O	495	N≡N	941
C-H	413	C-Cl	339	О-Н	467	I-I	149	C=O	745	C≡N	891
C-C	347	C-Br	276	O-O	146	S-H	347	C≡O	1072	C=N	615

### Specific Heat Capacities, c at SATP

Substance	J/(g•°C)	Substance	J/(g•°C)
aluminum	0.900	nickel	0.444
copper	0.385	silver	0.237
gold	0.129	tin	0.213
iron	0.444	zinc	0.388
lead	0.159	water	4.18

### Thermodynamic Properties of Organics At SATP

Substance	$\Delta \mathrm{H}_{\mathrm{f}}^{\circ}$	S°	Substance	$\Delta \mathrm{H}_{\mathrm{f}}^{\circ}$	S°
	(kJ•mol⁻¹)	$(J \bullet K^{-1} \bullet mol^{-})$		(kJ•mol <sup>-1</sup> )	$(J \bullet K^{-1} \bullet mol^{-1})$
benzene, $C_6H_{6(1)}$	+49.0	172.8	hexane, $n-C_6H_{14}$ (1)	-198.6	296.1
bromoethane, $CH_3CH_2Br_{(g)}$	-90.5		iodoethane, CH <sub>3</sub> CH <sub>2</sub> I <sub>(g)</sub>	-40.7	
bromomethane, CH <sub>3</sub> Br (g)	-37.2	246.3	iodomethane, CH <sub>3</sub> I (g)	-15.5	163.2
butanal, CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CHO <sub>(1)</sub>	-241.2		methanal, HCHO <sub>(g)</sub>	-108.7	218.7
butane, n-C <sub>4</sub> H <sub>10 (g)</sub>	-126.5	310.1	(formaldahyde)		
butan-1-ol, C <sub>4</sub> H <sub>9</sub> OH <sub>(1)</sub>	-327.4	228.0	methane, CH <sub>4</sub> (g)	-74.8	186.2
but-1-ene, C <sub>4</sub> H <sub>8 (g)</sub>	-0.4	305.6	methanoic acid, CH3OH(1)	-425.1	129.0
but-1-yne, $C_4H_6(g)$	+165.2		(formic)		
carbon tetrachloride, CCl <sub>4 (1)</sub>	-128.4	216.4	methanol, CH <sub>3</sub> OH <sub>(l)</sub>	-239.1	239.7
CCl <sub>4</sub> (g)	-96.0	309.9	methoxymethane, CH <sub>3</sub> OCH <sub>3</sub> (g)	-184.0	266.7
chloroethene, CH <sub>3</sub> CH <sub>2</sub> Cl <sub>(g)</sub>	-136.8	263.9	methylpropane, $C_4H_{10(g)}$	-134.5	294.6
chloromethane, CH <sub>3</sub> Cl <sub>(g)</sub>	-82.0	234.5	napthalene, C <sub>10</sub> H <sub>8 (s)</sub>	+77.7	
cyclopropane, (CH <sub>2</sub> ) <sub>3</sub> (g)	+53.3		octane, n- $C_8H_{18}$ (l)	-250.0	361.1
1,2-dichloroethane, (CH <sub>2</sub> Cl) <sub>2(g)</sub>	-165.0		pentane, n-C <sub>5</sub> H <sub>12</sub> (l)	-173.1	262.7
ethanal, CH <sub>3</sub> CHO <sub>(g)</sub>	-191.5	160.2	phenylethene or styrene	+103.8	345.1
ethane, $C_2H_6$ (g)	-83.8	229.5	phenol, $C_6H_5OH_{(S)}$	-165.0	
ethane-1,2-diol, (CH <sub>2</sub> OH) <sub>2(1)</sub>	-454.8	166.9	propanal, CH <sub>3</sub> CH <sub>2</sub> CHO <sub>(1)</sub>	-217.1	
ethanoic acid, CH <sub>3</sub> CO <sub>2</sub> H <sub>(1)</sub>	-484.5	159.8	propane, $C_3H_8$ (g)	-104.5	269.9
(acetic)	101.5	157.0	propanone(acetone)	-248.0	198.8
ethanol, C <sub>2</sub> H <sub>5</sub> OH <sub>(1)</sub>	-277.1	160.7	propan-1-ol, $C_3H_7OH_{(1)}$	-302.7	196.6
ethene, C <sub>2</sub> H <sub>4</sub> (g)	+52.5	219.5	propene, $C_3H_{6(g)}$	+20.2	266.9
ethoxyethane, (CH <sub>3</sub> CH <sub>2</sub> ) <sub>2</sub> O <sub>(g)</sub>	-279.0	251.9	propyne, $C_3H_4(g)$	+186.6	248.1
ethyne, $C_2H_2(g)$	+228.2	201.0	sucrose, $C_{12}H_{22}O_{11(s)}$	-2221.0	360.2
fluoromethane, CH <sub>3</sub> F $(g)$	-247.0		2,2,4-trimethyl pentane	-259.2	328.0
glucose, C <sub>6</sub> H <sub>12</sub> O <sub>6(s)</sub>	-1260.0	212.1	urea	-335.5	104.

Thermodynamic Properties of Inorganics At SATP)

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Substance	$\Delta H_{ m f}^{\circ}$	S°	$\Delta G_{ m f}$	Substance	$\Delta \mathrm{H}_{\mathrm{f}}^{\circ}$	S°	$\Delta G_{ m f}^{\circ}$
	(kJ•mol <sup>-1</sup> )		ol <sup>-1</sup> ) (kJ•mol <sup>-1</sup>				ol <sup>-1</sup> ) (kJ•mol <sup>-1</sup> )
$Al_{(S)}$	0	28.3	0	$Pb_{(s)}$	0	64.8	0
$Al_2O_3(s)$	-1675.7	50.9	-1582.3	PbCl <sub>2 (s)</sub>	-359.4	136.0	-314.1
$Al_2(SO_4)_3$ (s)	-3405.5	50.9	-1582.3	PbO (s)	-219.0	66.5	-188.6
BaCO <sub>3 (s)</sub>	-1216.3	112.1	-1142.0	$PbO_{2(s)}$	-277.4	68.6	
BaCl <sub>2 (s)</sub>	-860.2	124.1	-813.5	Mg(s)	0	32.7	0
BCl <sub>3</sub> (g)	-404	291.1	-390.1	MgCO <sub>3 (s)</sub>	-1095.8	65.7	
B <sub>2</sub> O <sub>3 (s)</sub>	-1273	54.18	-1144.1	$MgCl_{2(S)}$	-641.3	89.63	-591.8
Br <sub>2</sub> (1)	0	152	0	$Mg(OH)_{2(s)}$	-924.5	63.24	
Ca(s)	0	41.4	0	$MgO_{(s)}$	-601.6	26.95	-569.4
CaCO <sub>3 (s)</sub>	-1207	92.9	-1128.8	$N_{2(g)}$	0	191.6	0
CaBr <sub>2 (s)</sub>	-682.8	130.2	-1352.4	NH <sub>3</sub> (g)	-45.9	192.78	-16.5
CaCl <sub>2</sub> (s)	-795.8	104.6	-748.1	N <sub>2</sub> H <sub>4</sub> (1)	50.6	121.2	149.3
$CaO_{(S)}$	-634.9	38.1	-566.5		+95.4	237.11	
	-986.1	83.4	-900.5 -901.7	N2H4 (g)		94.6	-202.9
$Ca(OH)_{2(s)}$				NH4Cl <sub>(S)</sub>	-314.4		
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2 (s)</sub>	-4119	236.9	-3897.7	$NH_4NO_{3(s)}$	-365.6	151.08	-183.9
CaSO <sub>4 (s)</sub>	-1434.1	108.4	-1326.8	NO(g)	90.2	210.76	86.6
$C_{(s)}$ graphite	0	5.7	0	$NO_{2}(g)$	33.2	240.1	51.3
$C_{(s)}$ diamond	+1.88	2.38	+2.90	$N_2O_{(g)}$	82.1	219.9	104.2
$CO_{(g)}$	-110.5	197.66	-137.2	$N_2O_4(g)$	9.2	304.3	97.9
$CO_{2}(g)$	-393.5	213.78	-394.4	$O_{2(g)}$	0	205.1	0
$\text{Cl}_{2(g)}$	0	223.1	0	$O_{3(g)}$	142.7	238.9	163.2
Cu (s)	0	+33.2	0	PCl <sub>3 (g)</sub>	-319.7	217.2	
CuCl (s)	-137.2	86.2	-119.9	$PCl_{5(g)}$	-443.5	364.6	
CuCl <sub>2</sub> (s)	-220.1	108.1	-175.7	$K_{(s)}$	0	64.2	0
Cu <sub>2</sub> O <sub>(s)</sub>	-168.6	93.1	-146.6	KCl (s)	-436.7	82.55	-409.1
CuO (s)	-157.3	42.6	-129.7	KClO <sub>3</sub> (s)	-397.7	143.1	-296.3
CuSO <sub>4 (s)</sub>	-771.4	109.2	-663.6	KOH <sub>(s)</sub>	-424.8	78.9	-379.1
CuSO <sub>4</sub> ·5H <sub>2</sub> O <sub>s</sub> )	-2279	301.6	-1887.1	$Ag_{(s)}$	0	42.6	0
F <sub>2</sub> (g)	0	202.8	0	$AgBr_{(s)}$	-100.4	107.11	-97.4
$H_{2(g)}$	0	130.7	0	$AgCl_{(S)}$	-127.0	96.25	-109.8
$H_2O_{2(1)}$				$AgNO_{3(s)}$	-124.4	140.9	-33.4
	-187.8 -36.3	109.6 198.7	-120.4 -53.5	Ag2O (s)	-31.1	121.8	-11.3
HBr(g)				Na (s)	0	51.2	0
HCl (g)	-92.3	186.9	-95.3	NaBr <sub>(S)</sub>	-361.1	86.82	-350.2
HCl (aq)	-167.2	56.7	-131.8	$Na_2CO_3(s)$	-1130.7	135.0	-1044.0
$HCN_{(g)}$	+135.1	201.81	+125.2	NaCl <sub>(s)</sub>	-411.2	115.5	
HF(g)		+173.8	-273.2	NaF <sub>(s)</sub>	-571	51.7	-545.6
$HI_{(g)}$	+26.5	206.59	+1.75	NaOH (s)	-425.6	64.4	-379.5
$HNO_{3(l)}$	-174.1	155.6	-80.7		-287.8	98.50	-287.3
HNO <sub>3 (aq)</sub>	-207.0			NaI (s)			
$H_3PO_{4(s)}$	-1279.0	110.5	-1119.1	S <sub>8</sub> (s) rhombic	0	31.8	0
$H_2S_{(g)}$	-20.6	205.8	-33.6	$S_{(g)}$	278.8	167.8	283.3
H <sub>2</sub> SO <sub>4 (1)</sub>	-813.8	156.9	-690.0	$SO_{2}(g)$	-296.8	248.22	-300.2
H <sub>2</sub> SO <sub>4 (aq)</sub>	-909.3	20.16	-743.4	$SO_{3(g)}$	-395.7	256.8	-371.1
$I_{2(s)}$	0	116.3	0	$SnO_{(S)}$	-280.7	57.17	
I <sub>2 (g)</sub>	+62.4	180.79		$SnO_{2(s)}$	-577.6	49.04	
Fe (s)	0	27.8	0	H <sub>2</sub> O (1)	-285.8	69.95	-237.1
FeO (s)	-272.0	57.6	+245.1	$H_2O_{(g)}$	-241.8	188.84	-228.6
Fe <sub>2</sub> O <sub>3 (s)</sub>	-824.2	87.4	-742.2	$ZnO_{(8)}$	-350.5	43.65	
FeCl <sub>2 (s)</sub>	-341.8	118.0	-302.8	$ZnS_{(S)}$	-206.0	57.7	
FeCl <sub>3 (s)</sub>	-399.5	142.3	-344.0	<b>\'</b> /			
2 00.3 (S)	377.3	1.2.3	511.0				

# **<u>Heat and Calorimetry worksheet</u>**

Specific Heat Capacity,  $c_{\mbox{\scriptsize H}_2\mbox{\scriptsize O}}$  is 4.18 J/g °C

1.	How many joules are needed to warm 25.5 grams of water from 14°C to 22.5°C? (ans. 9.1 x 10 <sup>2</sup> J)
2.	Calculate the number of joules released when 75.0 grams of water are cooled from 100.0°C to 27.5°C. (ans. $2.27 \times 10^4  \mathrm{J}$ )
3.	If $1.13 \times 10^4$ J of heat is added to a water sample and the temperature rises from 88.0 °C to its boiling point, what mass of water is in the sample? (ans. 225 g )
4.	The specific heat capacity of gold is $0.128$ J/g °C. How much heat would be needed to warm 250.0 grams of gold from 25.0 °C to $100.0$ °C? (ans. $2.40 \times 10^3$ J)
5.	The specific heat capacity of zinc is 0.386 J/g $^{\circ}$ C . How many joules would be released when 454 grams of zinc at 96.0 $^{\circ}$ C were cooled to 28.0 $^{\circ}$ C? (ans. 1.19 x 10 <sup>4</sup> J)
6.	How much heat is absorbed by 2.50 x $10^2$ g of water and the 450. g Al can (c <sub>Al</sub> is 0.900 J/g °C ) when they are heated from 10.0 °C to 85.0 °C? (ans. 1.09 x $10^5$ J)
7.	What is the temperature change if 1.386 x $10^3$ J is absorbed by 60.0 g of copper which has a specific hear capacity of 0.385 J/g °C? (ans. 60.0 °C )

# **Molar Enthalpy**

1.	In a calorimetry experiment, 0.1277 g of Mg ribbon was added to 200.0 mL 0.500 M HCl at 24.12 °C. The water temperature increased to 27.10 °C. Calculate $\Delta H$ per mole of HCl. (ans: $-24.9$ kJ/mol HCl)
2.	A 54.7 g sample of arsenic tribromide was heated until the compound melted. The molten compound was then poured into a calorimeter containing 300.0 g water at 22.50 °C. When the last bit of the compound had solidified, the temperature of the water was 24.13 °C. This is called the molar heat of fusion of AsBr <sub>3</sub> . Calculate $\Delta H$ (per mole of AsBr <sub>3</sub> ) of: (ans.: -11.8 kJ/mol AsBr <sub>3</sub> )
3.	A 70.0 g sample of cesium is sealed in a glass vial and lowered into 250.0 mL of water at 90.00 °C. When the cesium had melted, the temperature of the water had dropped to 88.98 °C. Determine the molar heat of fusion for cesium. (ans.: +2.02 kJ/mol Cs)
4.	A 2.5 g sample of sucrose ( $C_{12}H_{22}O_{11}$ ) was burned in excess oxygen in a calorimeter which contained 2.19 kg of water. The temperature of the water increased from 20.50 °C to 25.01 °C. Determine the molar heat of combustion of sucrose. (ans.: $-5.7 \times 10^3$ kJ/mol $C_{12}H_{22}O_{11}$ )
5.	A 12.7 g sample of sulfur (S <sub>8</sub> ) is burned in a calorimeter. The calorimeter contains 2.20 kg of water at 21.08 °C. The reaction mixture is ignited and the temperature rises to 33.88 °C. From these data, calculate the molar heat of combustion of sulfur. (ans.: $-2.38 \times 10^3$ kJ/mol S <sub>8</sub> )
6.	The burning of 5.08 g benzene ( $C_6H_6$ ) releases enough heat to raise the temperature of 5.0 kg of water from 10.1 °C to 19.6 °C. Calculate the molar heat of combustion of benzene. (ans.: $-3.1 \times 10^3$ kJ/mol $C_6H_6$ )
7.	If 8.00 g ammonium nitrate is dissolved in 1.0 L water, the water decreases in temperature from 21.0 °C to 20.39 °C. Determine the molar heat of solution of the ammonium nitrate. (ans.: $+26$ kJ/mol NH <sub>4</sub> NO <sub>3</sub> )

### **Heats of Reaction**

Using the Standard values of  ${\rm H^{\circ}_f}$ , calculate the heats of reaction,  $\Delta {\rm H^{\circ}_{TXN}}$ , or heats of formation,  $\Delta {\rm H^{\circ}_f}$  All answers must include the intermediate steps with the formation reaction from the elements and their manipulation to form the overall reaction.

For #1-6, the equation:  $\Delta H_{rxn}^{\circ} = \Sigma n \Delta H_{f}^{\circ}_{products} - \Sigma n \Delta H_{f}^{\circ}_{reactants}$  CANNOT BE USED.

eg. 
$$SO_{2(g)}$$
 +  $H_2O_{(l)}$  +  $O_2$   $\rightarrow$   $H_2SO_{4(aq)}$   $\Delta H^{\circ}kJ$ 

(1) 
$$1/8 S_8 + O_2 \rightarrow SO_2$$
 -296.8

(2) 
$$H_2 + 1/2 O_2 \rightarrow H_2O$$
 -285.8

(3) 
$$H_2 + 2 O_2 + 1/8 S_8 \rightarrow H_2SO_4$$
 -909.3

Then multiply or reverse, whatever is needed so that they add to the original reaction.

1. 
$$C_6H_{6(1)}$$
 + 15/2  $O_{2(g)}$   $\rightarrow$  6  $CO_{2(g)}$  + 3  $H_2O_{(g)}$ 

2. 
$$2 \text{ HNO}_{3 \text{ (aq)}}$$
 +  $NO_{(g)}$   $\rightarrow$   $3 NO_{2 \text{ (g)}}$  +  $H_2O_{(l)}$ 

3. 
$$C_2H_2(g)$$
 +  $C_2H_6(g)$   $\rightarrow$  2  $C_2H_4(g)$ 

4. 
$$PbO_{2(s)}$$
 +  $CO_{(g)}$   $\rightarrow$   $PbO_{(s)}$  +  $CO_{2(g)}$ 

5. 
$$Al_2(SO_4)_3$$
 (s) +  $3 H_2O_{(1)}$   $\rightarrow$   $Al_2O_3$  (s) +  $3 H_2SO_4$  (aq)

6. 
$$3 \text{ SO}_{2 \text{ (s)}}$$
 +  $2 \text{ HNO}_{3 \text{ (aq)}}$  +  $2 \text{ H}_{2}\text{O}_{(1)}$   $\rightarrow$   $3 \text{ H}_{2}\text{SO}_{4 \text{ (aq)}}$  +  $2 \text{ NO}_{(g)}$ 

7. Given that  $\Delta H^{\circ}_{rxn} = -1196.0 \text{ kJ}$  for the following, calculate the  $\Delta H^{\circ}_{f}$  for ClF<sub>3</sub> (g).

$$2 \; \text{ClF}_{3 \; (g)} \qquad + \quad 2 \; \text{NH}_{3 \; (g)} \qquad \rightarrow \qquad \text{N}_{2 \; (g)} \quad + \qquad 6 \; \text{HF}_{\; (g)} \quad + \qquad \text{Cl}_{2 \; (g)}$$

8. Given that  $\Delta H^{\circ}_{rxn} = -52.3$  kJ for the following, calculate the  $\Delta H^{\circ}_{f}$  for HNO<sub>2</sub> (g).

$$HNO_{2(g)}$$
 +  $1/2 O_{2(g)}$   $\rightarrow$   $HNO_{3(aq)}$ 

9. Given that  $\Delta H^{\circ}_{rxn} = -386.2$  kJ for the following, calculate the  $\Delta H^{\circ}_{f}$  for Fe(CO)<sub>5</sub> (g).

$$Fe_2O_3(s)$$
 +  $13CO(g)$   $\rightarrow$   $2Fe(CO)_5(g)$  +  $3CO_2(g)$ 

10. Given that  $\Delta H^{\circ}_{rxn} = +47.2 \text{ kJ}$  for the following, calculate the  $\Delta H^{\circ}_{f}$  for Fe<sub>3</sub>O<sub>4 (s)</sub>.

$$2 \operatorname{Fe_3O_4}(s) + \operatorname{CO_2}(g) \rightarrow 3 \operatorname{Fe_2O_3}(s) + \operatorname{CO}(g)$$

# Hess' Law - Using Enthalpies of Formation and the Summation Formula worksheet

For the following equations, create the equations of formation and use the  $\Delta H_f^{\circ}$  values to calculate the  $\Delta H_{rxn}^{\circ}$ . Also for each question, use the Summation Formula (the one with  $\Sigma$  in it) to calculate the  $\Delta H_{rxn}^{\circ}$ .

1. Calcium carbonate decomposes at high temperature to form carbon dioxide and calcium oxide, calculate the enthalpy of reaction.

2. Carbon tetrachloride can be formed by reacting chlorine with methane, calculate the enthalpy of reaction.

 $CH_4$  +  $2 Cl_2$   $\rightarrow$   $CCl_4$  +  $2 H_2$ 

3. When potassium chloride reacts with oxygen under the right conditions, potassium chlorate is formed:

 $2 \text{ KCl} + 3 \text{ O}_2 \rightarrow 2 \text{ KClO}_3$ 

# Hess' Law Lab

These two reactions can be used to solve for the  $\Delta H_f$  for Ca(OH)<sub>2</sub> (s)

$$Ca(s) + O_2(g) + H_2(g) \rightarrow Ca(OH)_2(s)$$

#### **Data Provided:**

The following reactions occurred in a styrofoam calorimeter and the initial and maximum temperature was measured with a thermometer:

Reaction 1	Mass of Calcium	Mass of Water in Calorimeter	Initial T (°C)	Final T (°C)
Calcium reacting with Water	1.050 g	102.1 g	21.2	43.1
Reaction 2	Mass of Hydrogen			
Hydrogen gas reacting with excess Oxygen gas	0.028 g	102.1 g	21.2	30.5

### **Thinking and Investigation (Problem Solving)**

- 1. Write out balanced chemical equations for Reaction #1 and Reaction #2.
- 2. Using the given data, solve for the  $\Delta H_1$  for Reaction #1.
- 3. Using the given data, solve for the  $\Delta H_2$  for Reaction #2.
- 4. Are Reaction #1 and Reaction #2 exothermic or endothermic? Give reasons for your answer.
- 5. Give the thermochemical equations for Reaction #1 and Reaction #2.
- 6. Use the equation version of Hess's Law to solve for  $\Delta H_f$  for Ca(OH)2.
- 7. Calculate the percentage error if the theoretical value for  $\Delta H_f$  for Ca(OH) 2 is -986.09 kJ/mol.
- 8. Discuss what would happen if the calcium had reacted with oxygen prior to being put in the water in Reaction #1. Discuss in terms of  $\Delta H_1$ .
- 9. Discuss TWO possible sources of heat loss in this experiment. Indicate the impact of heat loss on the experiment.

#### Hess' Law with Given Equations Worksheet

1. a) Calculate the enthalpy change,  $\Delta H_{rxn}^{\circ}$ , for the following reaction using equations 1, 2 and 3.

$$3 N_2 H_4 (l) + 4 ClF_3 (g) \rightarrow 3 N_2 (g) + 12 HF (g) + 2 Cl_2 (g)$$

Given:  $\Delta H_{rxn}^{\circ} (kJ)$ 1)  $N_2H_4 + O_2 \rightarrow N_2 + 2H_2O$  - 622
2)  $2ClF_3 + 2NH_3 \rightarrow N_2 + 6HF + Cl_2$  - 1196
3)  $4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$  - 1530

- b) Use the summation formula and the  $\Delta H_{TXN}^{\circ}$  from (a) to determine the  $\Delta H_f^{\circ}$  of ClF3 .
- c) Predict the sign of  $\Delta Srxn^{\circ}$  and  $\Delta Grxn^{\circ}$ .
- 2. Calculate the enthalpy change,  $\Delta H_{rxn}^{\circ}$ , for the following reaction using equations 1, 2 and 3.

$$C(s, granite) + O_2(g) \rightarrow CO_2(g)$$

Given:  $\Delta H_{rxn}^{\circ} (kJ)$ 1)  $2Sr + 2C + 3O_2 \rightarrow 2SrCO_3$  - 2440
2)  $SrO + CO_2 \rightarrow SrCO_3$  - 234
3)  $2Sr + O_2 \rightarrow 2SrO$  - 1184

3. Calculate the enthalpy change,  $\Delta H_{rxn}^{\circ}$ , for the following reaction using the following equations:

$$2 B (s) + 3 H2 (g) \rightarrow B2H6 (g)$$

Given:  $\Delta H_{rxn}^{\circ} (kJ)$ 1) 2 B + 3/2 O<sub>2</sub>  $\rightarrow$  B<sub>2</sub>O<sub>3</sub> - 1273.0 2) B<sub>2</sub>H<sub>6</sub> + 3 O<sub>2</sub>  $\rightarrow$  B<sub>2</sub>O<sub>3</sub> + 3 H<sub>2</sub>O (g) - 2035.0 3) H<sub>2</sub> + 1/2 O<sub>2</sub>  $\rightarrow$  H<sub>2</sub>O (l) - 285.8 4) H<sub>2</sub>O (l)  $\rightarrow$  H<sub>2</sub>O (g) + 44.0

4. a) Calculate the enthalpy change,  $\Delta H_{rxn}^{\circ}$ , for the following reaction using equations 1, 2 and 3.

$$3\;NO_{2}\left(g\right)\;\;+\;\;H_{2}O\left(l\right)\;\;\rightarrow\;\;2\;HNO_{3}\left(aq\right)\;\;+\;\;NO\left(g\right)$$

- b) Use the summation formula to calculate the  $\Delta H_{\text{TX}\text{N}}{}^{\circ}$  for (a)
- c) Predict the sign of  $\Delta Srxn^{\circ}$  and  $\Delta Grxn^{\circ}$ .

5. Calculate the enthalpy change,  $\Delta H_{rxn}^{\circ}$ , for the following reaction using the following equations:

$$P_4O_{10}(s) + 6PCl_5(g) \rightarrow 10Cl_3PO(g)$$

Given: 
$$\Delta H_{rxn}^{\circ} (kJ)$$
1)  $P_4 + 6 Cl_2 \rightarrow 4 PCl_3 - 1225.6$ 
2)  $P_4 + 5 O_2 \rightarrow P_4O_{10} - 2967.3$ 
3)  $PCl_3 + Cl_2 \rightarrow PCl_5 - 84.2$ 
4)  $PCl_3 + 1/2 O_2 \rightarrow Cl_3PO - 285.7$ 

6. Calculate the enthalpy change,  $\Delta H_{rxn}^{\circ}$ , for the following reaction using the following equations:

$$2 \text{ Al (s)} + 3 \text{ Cl}_2(g) \rightarrow 2 \text{ AlCl}_3(s)$$

7. Calculate the enthalpy change,  $\Delta H_{TXN}^{\circ}$ , for the formation of HNO<sub>2</sub> using the following equations:

8. Acetylene,  $C_2H_2$ , is a gas commonly used in welding. It is formed in the reaction of calcium carbide,  $CaC_2$ , with water. Given the thermochemical equations below, calculate the value of  $\Delta H_f$   $^{\circ}$  for acetylene in units of kilojoules per mole:

Given: 
$$\Delta H_{\text{rxn}}^{\circ} \text{ (kJ)}$$
1) CaO + H<sub>2</sub>O  $\rightarrow$  Ca(OH)<sub>2</sub> -65.3  
2) 2 CaO 5 C  $\rightarrow$  2 CaC<sub>2</sub> + CO<sub>2</sub> +753.0  
3) + CaCO<sub>3</sub>  $\rightarrow$  CaO + CO<sub>2</sub> +178.0  
4) CaC<sub>2</sub> 2 H<sub>2</sub>O  $\rightarrow$  Ca(OH)<sub>2</sub> + C<sub>2</sub>H<sub>2</sub> -126.0  
5) C + O<sub>2</sub>  $\rightarrow$  CO<sub>2</sub> -393.5  
6) 2 H<sub>2</sub>O  $\rightarrow$  2 H<sub>2</sub> + O<sub>2</sub> +571.6

# Hess' Law with Bond Energies/Enthalpies Worksheet

Hess' Law for bond enthalpies is:

$$\Delta H_{rxn}^{\circ} = \Sigma BE_{reactant \ bonds \ broken} - \Sigma BE_{product \ bonds \ broken}$$

Use the Bond Energy values from the Reference Sheet

eg. Hydrogenation of double and triple bonds is an important industrial process. Calculate (in kJ) the standard enthalpy change  $\Delta H$  for the hydrogenation of ethyne (acetylene) to ethane:

$$H-C\equiv C-H(g) + 2H_2(g) \rightarrow H_3C-CH_3(g)$$

 $\Delta H_{rxn}^{\circ} = \Sigma BE_{reactant \ bonds \ broken} - \Sigma BE_{product \ bonds \ broken}$ 

- = [2 C-H bonds + 1 C≡C bond + 2 H-H bonds] [6 C-H bonds + 1 C-C bond
- = [2 mol(413 kJ/mol) + 1 mol(839 kJ/mol) + 2 mol(432 kJ/mol)] [6 mol(413 kJ/mol) + 1 mol(347 kJ/mol)]
- = 2529 kJ 2825 kJ
- = -296 kJ

OR = 
$$[1 \text{ C} \equiv \text{C bond} + 2 \text{ H} - \text{H bonds}] - [4 \text{ C} - \text{H bonds} + 1 \text{ C} - \text{C bond}] = -296 \text{ kJ}$$

1. Using bond enthalpies, calculate the reaction enthalpy ( $\Delta H$ ) for:

$$CH_{4}\left(g\right) \quad + \quad Cl_{2}\left(g\right) \quad \rightarrow \quad CH_{3}Cl\left(g\right) \quad + \quad HCl\left(g\right)$$

2. Calculate  $\Delta H$  for this reaction:

$$\text{H}_2\text{C=CH}_2\left(g\right) \quad + \quad \text{H}_2\text{O}\left(l\right) \quad \rightarrow \quad \text{CH}_3\text{-CH}_2\text{-OH}\left(l\right)$$

3. Calculate  $\Delta H$  for this reaction:

$$2 \text{ CH}_3\text{OH (l)} + 3 \text{ O}_2(g) \rightarrow 2 \text{ CO}_2(g) + 4 \text{ H}_2\text{O}(g)$$

4. Calculate the bond energy of the Cl-F bond using the following data:

$$\text{Cl}_2 + \text{F}_2 \rightarrow 2\text{ClF}$$
  $\Delta \text{H}_{rxn}^{\circ} = -108 \text{ kJ}$ 

5. Ammonia reacts with oxygen to form nitrogen dioxide and steam, as follows:

$$4\;NH_{3}\left(g\right)\quad+\quad7\;O_{2}\left(g\right)\quad\rightarrow\quad4\;O-N=O\left(g\right)\quad+\quad6H_{2}O\left(g\right)$$

6. Calculate  $\Delta H$  for this reaction:

$$2 \text{ CH}_3\text{CH}=\text{CH}_2 + 9 \text{ O}_2 \rightarrow 6 \text{ CO}_2 + 6 \text{ H}_2\text{O}$$

7. Considering bonds broken and formed ONLY, what is the enthalpy change for the following reaction:

$$C_{40}H_{82} \rightarrow C_{16}H_{34} + 2C_{12}H_{24}$$
 (cyclic)

# **Thermochemistry Questions**

1. a) Urea (from urine),  $CO(NH_2)_{2(aq)}$ , hydrolyzes slowly in the presence of water to produce ammonia and carbon dioxide. What is the standard  $\Delta H_{rxn}^{\circ}$ ,  $\Delta S_{rxn}^{\circ}$  and  $\Delta G_{rxn}^{\circ}$  for this reaction when 1 mole of urea reacts with water? (Create the balanced equation first then use the summation formulas and the formation values from the reference booklet.)

b) At what temperature is this reaction spontaneous?

2. What is  $\Delta G_{rxn}^{\circ}$  for the combustion of liquid ethyl alcohol (C<sub>2</sub>H<sub>5</sub>OH) to give CO<sub>2(g)</sub> and H<sub>2</sub>O<sub>(g)</sub>? Is the reaction spontaneous? ( $\Delta S^{\circ}$  C<sub>2</sub>H<sub>5</sub>OH = 160.7 J• K<sup>-1</sup>•mol<sup>-1</sup>)

3. Calculate  $\Delta H_{rxn}^{\circ}$  and  $\Delta S_{rxn}^{\circ}$  for the following reaction and decide in which direction each of these factors will drive the reaction.

$$\mathrm{N}_{2(g)} \quad + \quad 3 \ \mathrm{H}_{2(g)} \quad \rightarrow \quad 2 \ \mathrm{NH}_{3(g)}$$

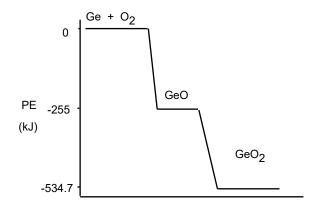
#### SUPPLEMENTARY ENTHALPY PROBLEMS

1. Construct an enthalpy diagram showing the enthalpy changes for a one step conversion of germanium,  $Ge_{(S)}$ , into  $GeO_{2(S)}$  and a two step conversion - first to the monoxide,  $GeO_{(S)}$  followed by the oxidation to  $GeO_{2(S)}$ . The relevant thermochemical equations are as follows;

$$Ge(s) + 1/2 O_{2(g)} \rightarrow GeO(s)$$
  $\Delta H^{\circ} = -255 \text{ kJ}$   
 $Ge(s) + O_{2(g)} \rightarrow GeO_{2(s)}$   $\Delta H^{\circ} = -534.7 \text{ kJ}$ 

Using this diagram, determine the value of  $\Delta H^{\circ}$  for the reaction

$$GeO_{(S)} + 1/2 O_{2(g)} \rightarrow GeO_{2(S)}$$



2. Nitrogen monoxide oxidizes to the toxic red brown gas nitrogen dioxide in air. Construct an accurate enthalpy diagram for this reaction. Use the diagram to explain which of the oxides of nitrogen has stronger covalent bonds.

$$2 \text{ NO}(g) + O_2(g) \rightarrow 2 \text{ NO}_2(g)$$

3. One of the "building blocks" for proteins such as those in muscles and in sinews, is an amino acid called glycine, C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub>. The equation for its combustion is

$$4 \, \mathrm{C_2H_5NO_2}\,_{(8)} \quad + \quad 9 \, \mathrm{O_2}\,_{(g)} \quad \longrightarrow \quad 8 \, \mathrm{CO_2}\,_{(g)} \quad + \quad 10 \, \mathrm{H_2O}_{(l)} \quad + \quad 2 \, \mathrm{N_2}\,_{(g)}$$

The value of its  $\Delta H^{\circ}_{comb}$  is -973.49 kJ/mol. Calculate  $\Delta H_{f}^{\circ}$  for glycine.

4. On Easter Sunday, April 3, 1983, nitric acid spilled from a tank car near Denver, Colorado. The spill was neutralized with sodium carbonate. The reaction is

$$2 \text{ HNO3 (aq)} + \text{Na2CO3 (s)} \rightarrow 2 \text{ NaNO3 (aq)} + \text{H2O(l)} + \text{CO2 (g)}$$

- (a) Calculate  $\Delta H^{\circ}$  for this reaction.  $\Delta H_{f}^{\circ}$  for NaNO3 (aq) is -467 kJ/mol,  $\Delta H_{f}^{\circ}$  for HNO3 (aq) is -207.16 kJ/mol,  $\Delta H_{f}^{\circ}$  for Na2CO3 (aq) is -1129.60 kJ/mol]
- (b) Approximately 9.1 x 10<sup>4</sup> L of nitric acid was spilled. Assuming a molar concentration of 15.4M, how much sodium carbonate was required for complete neutralization and how much heat was evolved.
- (c) According to the Denver Post for April 4, 1983, authorities feared a volatile reaction might occur during the neutralization. Considering the magnitude of ΔH°, what was their major concern?
- (d) Predict the sign of  $\Delta Srxn^{\circ}$  and  $\Delta Grxn^{\circ}$ .

#### **KINETICS - Rate laws**

1. Using the data provided below, draw a Born-Haber cycle for the formation of lithium fluoride and calculate the enthalpy of formation of the compound

$$\text{Li}_{(s)}$$
 +  $^{1}/_{2} \text{F}_{2(g)}$   $\rightarrow$   $\text{LiF}_{(s)}$ 

Given:  $\Delta H$  vap (Li metal) = 155 kJ/mol BE of F-F = 150 kJ/mol 1st IE of Li atom = 520 kJ/mol E.A. of F atom = 333 kJ

 $1^{st}$  IE of Li atom = 520 kJ/mol E.A. of F atom = 333 kJ/mol Lattice energy = 1012 kJ/mol

2. Draw a Bohr-Haber cycle for the following reaction:

$$H_2O_{(l)} \rightarrow H_2_{(g)} + \frac{1}{2}O_2_{(g)}$$

Given: BE for H-H = 431. kJ/molBE for H-O = 458.9 kJ/mol BE for O=O = 485. kJ/mol  $\Delta H_{\text{Vap}}$  for water = 40.65 kJ/mol

3. For the reaction:  $2 \text{ NO } (g) + \text{H}_2 (g) \rightarrow \text{N}_2 \text{O} (g) + \text{H}_2 \text{O} (g)$  the following data was obtained:

Trial	[ <b>NO</b> ] <sub>i</sub> (mol / L)	[ <b>H</b> <sub>2</sub> ] <sub>i</sub> (mol / L)	Initial Rate (mol / L•s)
1	0.150	0.800	0.500
2	0.0750	0.800	0.125
3	0.150	0.400	0.250

- a) What is the rate law for the reaction?
- b) What is the value of the rate constant?
- c) What is the rate when the [NO] is 0.300 mol/L and [H<sub>2</sub>] is 0.400 mol/L?
- 4. For the reaction:  $O_{3(g)} + NO_{(g)} \rightarrow O_{2(g)} + NO_{2(g)}$  the following data was obtained:

Trial	<b>Frial</b> $[\mathbf{O}_3]_i \pmod{/} [\mathbf{NO}]_i \pmod{/}$		<b>Initial Rate of Formation of NO</b> <sub>2</sub> (mol / L•s)
	L)		
1	0.0010	0.0010	X
2	0.0010	0.0020	2x
3	0.0020	0.0010	2x
4	0.0020	0.0020	4x

What is the rate law for the reaction?

5. Write the following for the reaction

$$N_2 + 3H_2 \rightarrow 2NH_3$$

- a) The rate expression for the reaction (assume this reaction is elementary, only occurs in 1 step.)
- b) The order of the reaction for each reactant
- c) The overall order of the reaction

6. The rate constant for the reaction

$$HNO_3 + NH_3 \rightarrow NH_4NO_3$$

is 14.5 L/(mol.sec). If the concentration of the nitric acid is 0.050 M and the concentration of the ammonia is 0.10 M, what will the rate of this *elementary* reaction be?

7. For the reaction:  $5 \text{ Br}^-\text{ (aq)} + \text{ BrO}_3^-\text{ (aq)} + 6 \text{ H}^+\text{ (aq)} \rightarrow 3 \text{ Br}_2\text{ (l)} + 3 \text{ H}_2\text{O (l)}$ 

the following data was obtained at 298 K:

Trial	[Br <sup>-</sup> ] <sub>i</sub> (mol/L)	[BrO <sub>3</sub> -] <sub>i</sub> (mol /L)	[H <sup>+</sup> ] <sub>i</sub> (mol/L)	Initial Rate of Disappearance of BrO <sub>3</sub> <sup>-</sup> (mol/L•s)
1	0.00100	0.00500	0.100	2.50 x 10 <sup>-4</sup>
2	0.00200	0.00500	0.100	5.00 x 10 <sup>-4</sup>
3	0.00100	0.00750	0.100	3.75 x 10 <sup>-4</sup>
4	0.00100	0.01500	0.200	3.00 x 10 <sup>-3</sup>

- a) Determine the order of the reaction for each reactant.
- b) Write the rate law for the overall reaction.
- c) Determine the value of the specific rate constant for the reaction at 298 K.
- 8. When two compounds, A and B, are mixed together, they form the compound C, by a reaction that is not well understood. Fortunately, the following rate information was experimentally determined, as shown below:

A (mol/L)	B (mol/L)	Rate (mol/(L sec))
0.050	0.050	4.0 x 10 <sup>-3</sup>
0.100	0.050	8.0 x 10 <sup>-3</sup>
0.050	0.100	1.6 x 10 <sup>-2</sup>

- a) Determine the rate expression for this reaction.
- b) Determine the rate constant for this reaction with units.

#### **KINETICS - Rate Mechanisms and the RDS**

1. For the following reaction,

$$NO_{(g)} + O_{3(g)} \rightarrow NO_{2(g)} + O_{2(g)}$$

Given:  $E_{a(forward)} = 10.0 \text{ kJ/mol}$  and  $\Delta H \text{ (forward)} = -200.0 \text{ kJ/mol}$ 

- a) Draw the energy level diagram for this reversible reaction.
- b) Calculate the  $E_{a(reverse)}$  and the  $\Delta H$  (reverse).

For the reaction the following data was obtained:

Trial	[O <sub>3</sub> ] <sub>i</sub> (mol / L)	[ <b>NO</b> ] <sub>i</sub> (mol / L)	<b>Initial Rate of Formation of NO</b> <sub>2</sub> (mol / L•s)
1	0.0010	0.0010	X
2	0.0010	0.0020	2x
3	0.0020	0.0020	4x

- c) What is the rate law for the reaction?
- d) The proposed mechanism is 3-step. The 1<sup>St</sup> is the RDS producing O• and NO<sub>3</sub>, which are both rxn intermediates. Derive the other 2 elementary steps for the mechanism.
- 2. For the reaction:  $2 \text{ NO}_{(g)} + \text{Br}_{2(g)} \rightarrow 2 \text{ NOBr}_{(g)}$  the following data was obtained:

Trial	$[NO]_i \pmod{/L}$	$[\mathbf{Br}_2]_i \pmod{/L}$	Initial Rate of Formation of NOBr (mol / L•s)
1	0.0160	0.0120	3.24 x 10 <sup>-4</sup>
2	0.0160	0.0240	6.48 x 10 <sup>-4</sup>
3	0.0320	0.0060	6.48 x 10 <sup>-4</sup>

- a) Write the rate law equation that is consistent with the data.
- b) Calculate the value of the specific rate constant, k, and specify units.
- c) The following mechanism was proposed for the reaction:

$$\operatorname{Br}_{2\,(g)}$$
 +  $\operatorname{NO}_{(g)}$   $\rightarrow$   $\operatorname{NOBr}_{2\,(g)}$   $slow$   
 $\operatorname{NOBr}_{2\,(g)}$  +  $\operatorname{NO}_{(g)}$   $\rightarrow$   $2\operatorname{NOBr}_{(g)}$   $fast$ 

Is this mechanism consistent with the given experimental observations? Justify your answer.

3. The reaction:

$$NO_{2(g)} + CO_{(g)} \rightarrow NO_{(g)} + CO_{2(g)}$$

is believed to occur by the following reaction mechanism:

$$NO_{2(g)}$$
 +  $NO_{2(g)}$   $\rightarrow$   $NO_{3(g)}$  +  $NO_{(g)}$  (slow)  
 $NO_{3(g)}$  +  $CO_{(g)}$   $\rightarrow$   $NO_{2(g)}$  +  $CO_{2(g)}$  (fast)

- a) What is the rate law according to this mechanism?
- b) What would be the rate law if the reaction occurred directly in a single step?

4. Propose a mechanism for the chain reaction:

$$H_{2(g)} + I_{2(g)} \rightarrow 2HI_{(g)}$$

Where, I•, is a catalyst. Label each step as either chain initiation, propagation or termination.

5. Propose a mechanism for the chain reaction:

$$H_{2(g)} + I_{2(g)} \rightarrow 2HI_{(g)}$$

Where,  $I^{\bullet}$ , is a reaction intermediate. Label each step as either chain initiation, propagation or termination.

6. Draw an energy level diagram for:

$$X + Y \rightarrow Z$$

using the following information:

- a) The reaction is reversible
- b) The reaction consists of three elementary steps
- c) The rate determining step is the second step
- d) The forward reaction is endothermic
- e) The  $E_a$  is twice the  $\Delta H$  for the forward reaction.

## Thermochemistry Review Problems

- 1. A 2.50 g sample of sucrose ( $C_{12}H_{22}O_{11}$ ) was burned in excess oxygen under a 60.0 g Al calorimeter which contained 2.19 kg of water. The temperature of the water increased from 20.5 °C to 25.0 °C. Determine the molar heat of combustion of sucrose.
- 2. a) Calculate the enthalpy change,  $\Delta H_{rxn}^{\circ}$ , for the following reaction using equations 1, 2 and 3.

FeO + CO 
$$\rightarrow$$
 Fe + CO<sub>2</sub>

Given:  $\Delta H_{rxn}^{\circ}(kJ)$ 

1) Fe<sub>2</sub>O<sub>3</sub> + 3 CO  $\rightarrow$  2 Fe + 3 CO<sub>2</sub>

2) 3 Fe<sub>2</sub>O<sub>3</sub> + CO  $\rightarrow$  2 Fe<sub>3</sub>O<sub>4</sub> + CO<sub>2</sub>

3) Fe<sub>3</sub>O<sub>4</sub> + CO  $\rightarrow$  3 FeO + CO<sub>2</sub>

+38

- b) Calculate the enthalpy change,  $\Delta H_{rxn}^{\circ}$ , for the above using equations of formation and  $\Delta H_f^{\circ}$ .
- c) Using the Summation Formulas, calculate the  $\Delta H_{rxn}^{\circ}$ ,  $\Delta S_{rxn}^{\circ}$ ,  $\Delta G_{rxn}^{\circ}$  and determine the temperature where this reaction is spontaneous.
- 3. a) Calculate the enthalpy change,  $\Delta H_{rxn}^{\circ}$ , for the following using formation equations and  $\Delta H_f^{\circ}$ .

$$3 \text{ N}_2\text{H}_4(g) + 4 \text{ ClF}_3(g) \rightarrow 3 \text{ N}_2(g) + 12 \text{ HF}(g) + 2 \text{ Cl}_2(g)$$
  
$$\Delta \text{H}_f^{\circ}(\text{ ClF}_3) = -158.87 \text{ kJ/mol}$$

- b) Predict the sign of  $\Delta Srxn^{\circ}$  and  $\Delta Grxn^{\circ}$ .
- 4. Calculate the enthalpy change,  $\Delta H_{rxn}^{\circ}$ , for the following reaction using equations 1, 2 and 3.

- 5. Using the average bond energies, N $\equiv$ N (941 kJ/mol), N=N (418 kJ/mol), N-N (160 kJ/mol), N-H (391 kJ/mol) and H-H (432 kJ/mol) estimate the  $\Delta H_f^{\circ}$  for hydrazine, N<sub>2</sub>H<sub>4</sub>.
- 6. The  $\Delta H_{TX\Pi}{}^{\circ}$  of the gaseous reaction:

$$XeF_2 + H_2 \rightarrow 2HF + Xe$$

is found to be  $-430 \, \text{kJ}$ . Use this value and average bond energies [H-F (565 kJ/mol)] to determine the average bond energy of the Xe-F bond.

#### **KINETICS - REVIEW**

1. At high temperatures, the following reaction occurs:

$$4 \text{ NH}_{3 (g)} + 5 \text{ O}_{2 (g)} \rightarrow 4 \text{ NO}_{(g)} + 6 \text{ H}_{2} \text{O}_{(g)}$$

One experiment showed a concentration of ammonia of 0.120 mol/L at 10 s and of 0.100 mol/L at 55 s. Calculate the average rate, over this time interval, for each of the following:

- a) the rate of decomposition of NH<sub>3</sub>.
- b) the rate of production of water.
- c) the rate of production of NO.
- d) the rate of consumption of oxygen.
- 2. For the following reactions,

For the following reaction and its reverse activation energies were determined as follows:

$$C_2H_{4(g)} + H_{2(g)} \rightarrow C_2H_{6(g)}$$
  $E_a = 180 \text{ kJ/mol}$   $C_2H_{6(g)} \rightarrow C_2H_{4(g)} + H_{2(g)}$   $E_a = 317 \text{ kJ/mol}$ 

Calculate ΔH for the reaction of C<sub>2</sub>H<sub>4</sub> with hydrogen

3. For the reaction:

$$2 A + 2 B \rightarrow C + D$$

The following data about the reaction above were obtained from three experiments:

Experiment	[A] mol/L	[B] mol/L	Rate of Formation of C (mol/L •min)
1	0.60	0.15	$6.3x10^{-3}$
2	0.20	0.60	$2.8 \times 10^{-3}$
3	0.20	0.15	$7.0x10^{-4}$

- a) What is the rate equation for the reaction?
- b) What is the numerical value of the rate constant k? What are its dimensions?
- c) Propose a reaction mechanism for this reaction.

4. The following results were obtained when the reaction represented below was studied at 25°C.

$$2 \, \text{ClO}_{2(g)} \quad + \quad F_{2(g)} \quad \rightarrow \quad 2 \, \text{ClO}_2 F_{(g)}$$

Experiment	[ClO <sub>2</sub> ] <sub>i</sub> (mol/L)	$[F_2]_i \text{ (mol/L)}$	Rate of Increase of [ClO <sub>2</sub> F] <sub>i</sub> (mol/L •s)
1	0.010	0.10	2.4 10-3
2	0.010	0.40	9.6 10-3
3	0.020	0.20	9.6 10-3

a) Write the rate law expression for the reaction above.

b) Calculate the numerical value of the rate constant and specify the units.

c) In experiment 2, what is the initial rate of decrease of [F<sub>2</sub>]?

d) Which of the following reaction mechanisms is consistent with the rate law developed in (a). Justify your choice.

I. 
$$ClO_2 + F_2 \rightarrow ClO_2F_2$$
 (fast)

$$ClO_2F_2 \quad \rightarrow \quad ClO_2F \quad + \quad F \qquad \qquad (slow)$$

$${\rm ClO}_2 \quad + \quad {\rm F} \quad \rightarrow \quad {\rm ClO}_2 {\rm F} \qquad \qquad ({\rm fast})$$

II. 
$$F_2 \rightarrow 2 F$$
 (slow)  
  $2 (ClO_2 + F \rightarrow ClO_2F) (fast)$ 

5. Freon gases, e.g.  $CCl_2F_{2(g)}$ , from leaking air conditioners and refrigeration units also make their way into the upper atmosphere. These gases catalyze the destruction of ozone.

$$CCl_2F_{2(g)} + O_{3(g)} \rightarrow CClF_{2(g)} + ClO_{(g)} + O_{2(g)}$$

Where, Cl<sup>•</sup>, is a reaction intermediate. Propose a mechanism for this reaction.

6. Draw a potential energy diagram for the reaction

$$X + Y \rightarrow Z$$

showing the following information.

- (a) The mechanism consists of two elementary steps.
- (b) The second elementary step is the rate-determining step.
- (c) The overall reaction is exothermic.

- (d) What would happen to the shape of the graph if a catalyst were added?
- 7. Draw the Born-Haber cycle for the following reaction:

$$2 CO_{(g)} + O_{2(g)} \rightarrow 2 CO_{2(g)}$$