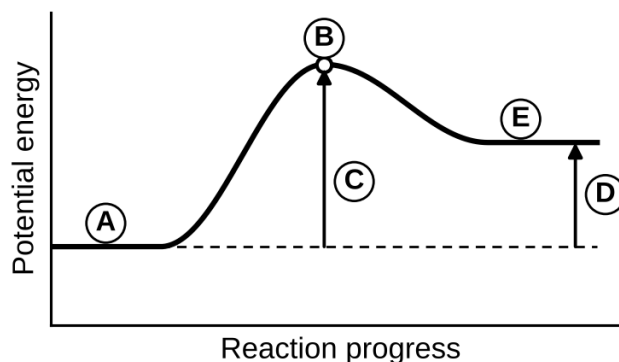


Show all work with units and correct significant figures.

|                      |                                                                                                                    |                                                              |                                                                                   |
|----------------------|--------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------|-----------------------------------------------------------------------------------|
| <b>Heat</b>          | $q = mc\Delta T$ , $\Delta T = T_{\text{final}} - T_{\text{initial}}$                                              | $q = m\Delta H_{\text{fus}}$ or $q = m\Delta H_{\text{vap}}$ | $q_{\text{rxn}} = -q_{\text{soln}}$ ; $\Delta H = q_{\text{rxn}} \div \text{mol}$ |
| <b>Energy</b>        | $\Delta G = \Delta H - T\Delta S$                                                                                  | $K = ^\circ\text{C} + 273$                                   | $1 \text{ kJ} = 1000 \text{ J}$                                                   |
| <b>Formation</b>     | $\Delta H^\circ_{\text{rxn}} = \sum n\Delta H^\circ_f(\text{products}) - \sum n\Delta H^\circ_f(\text{reactants})$ |                                                              |                                                                                   |
| <b>Water</b>         | $c_{\text{water}} = 4.18 \text{ J/g}\cdot^\circ\text{C}$                                                           | $c_{\text{ice}} = 2.06 \text{ J/g}\cdot^\circ\text{C}$       | $c_{\text{steam}} = 1.99 \text{ J/g}\cdot^\circ\text{C}$                          |
| <b>Water (phase)</b> | $\Delta H_{\text{fus}} = 334 \text{ J/g}$                                                                          | $\Delta H_{\text{vap}} = 2260 \text{ J/g}$                   | density = 1.00 g/mL                                                               |
| <b>Metals (c)</b>    | aluminum 0.897 J/g $\cdot^\circ\text{C}$                                                                           | iron 0.449 J/g $\cdot^\circ\text{C}$                         | copper 0.385 J/g $\cdot^\circ\text{C}$                                            |

## Part 1. PE Diagrams

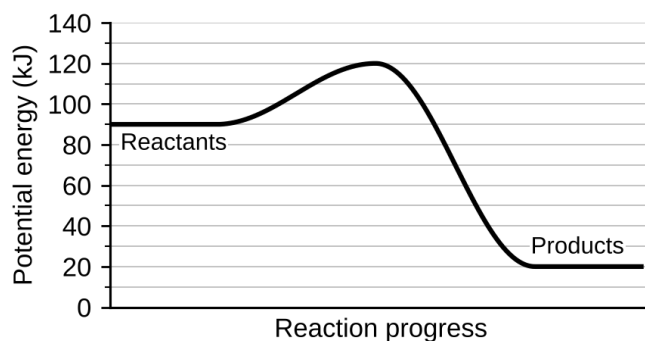
1. Identify what each letter on the PE diagram represents. Then decide if the reaction is exothermic or endothermic.



| Letter | What it represents                         | Letter       | What it represents                                            |
|--------|--------------------------------------------|--------------|---------------------------------------------------------------|
| A      | <i>PE of the reactants</i>                 | B            | <i>activated complex (transition state)</i>                   |
| C      | <i>activation energy, <math>E_a</math></i> | D            | <i><math>\Delta H</math>, the enthalpy change</i>             |
| E      | <i>PE of the products</i>                  | Exo or endo? | <i>endothermic (products higher, <math>\Delta H +</math>)</i> |

Both  $E_a$  (C) and  $\Delta H$  (D) are measured starting from the reactant line.

2. Use the PE diagram below.



(a) Find  $\Delta H$  for the reaction.

$$\Delta H = PE_{\text{products}} - PE_{\text{reactants}} = 20 \text{ kJ} - 90 \text{ kJ} = -70 \text{ kJ}$$

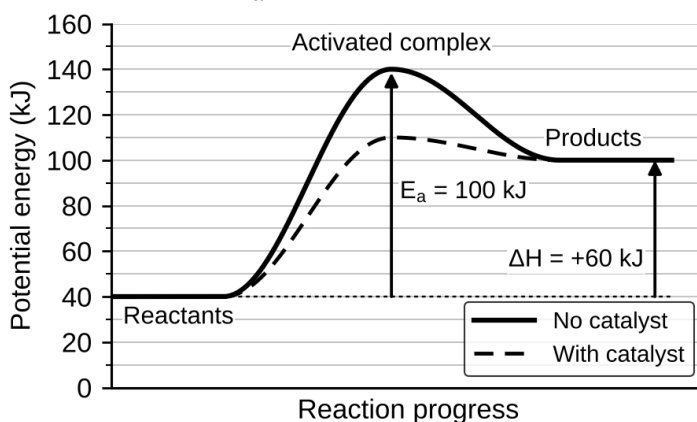
(b) Find the activation energy,  $E_a$ .

$E_a = PE_{\text{peak}} - PE_{\text{reactants}} = 120 \text{ kJ} - 90 \text{ kJ} = \mathbf{30 \text{ kJ}}$ .  $E_a$  is measured from the reactant line, not from zero.

(c) Is the reaction exothermic or endothermic? Give two pieces of evidence.

**Exothermic**. The products are lower than the reactants, and  $\Delta H$  is negative, so heat is released.

3. A reaction has reactants at 40 kJ,  $\Delta H = +60 \text{ kJ}$ , and  $E_a = 100 \text{ kJ}$ .



(a) Find the potential energy of the products and of the activated complex.

Products = 40 kJ + 60 kJ = **100 kJ**. Peak = 40 kJ + 100 kJ = **140 kJ**.

(b) Draw the PE diagram on the grid. Label the reactants, products, activated complex,  $E_a$ , and  $\Delta H$ .

See the solid curve: flat at 40 kJ, peak at 140 kJ, flat at 100 kJ. Both arrows start at the reactant line.

(c) A catalyst lowers  $E_a$  to 70 kJ. Draw the catalyzed path as a dashed curve on the same grid. Does the catalyst change  $\Delta H$ ? Explain.

The dashed curve peaks at 40 kJ + 70 kJ = 110 kJ.  **$\Delta H$  does not change** (still +60 kJ): a catalyst only lowers the hill, and the reactant and product lines stay the same.

## Part 2. Heat Calculations

4. How much heat is needed to warm 350. g of water from 18.0 °C to 75.0 °C? Give your answer in J and kJ.

$\Delta T = 75.0 \text{ °C} - 18.0 \text{ °C} = 57.0 \text{ °C}$ .  $q = mc\Delta T = (350. \text{ g})(4.18 \text{ J/g} \cdot \text{°C})(57.0 \text{ °C}) = 83,391 \text{ J} = \mathbf{8.34 \times 10^4 \text{ J} = 83.4 \text{ kJ}}$ . Positive, because the water absorbs heat.

5. A 45.0 g sample of a metal absorbs 1.21 kJ of heat and warms from 22.0 °C to 52.0 °C. Find its specific heat and use the reference table to identify the metal.

$q = 1.21 \text{ kJ} \times 1000 = 1210 \text{ J}$ ;  $\Delta T = 30.0 \text{ °C}$ .  $c = q \div (m\Delta T) = 1210 \text{ J} \div [(45.0 \text{ g})(30.0 \text{ °C})] = \mathbf{0.896 \text{ J/g} \cdot \text{°C}}$ , which matches **aluminum** (0.897).

6. 200. g of water at 85.0 °C releases 12.5 kJ of heat. What is its final temperature?

$q = -12,500 \text{ J}$  (heat released).  $\Delta T = q \div (mc) = -12,500 \text{ J} \div [(200. \text{ g})(4.18 \text{ J/g} \cdot \text{°C})] = -15.0 \text{ °C}$ .  $T_f = 85.0 \text{ °C} + (-15.0 \text{ °C}) = \mathbf{70.0 \text{ °C}}$ . Lower, because the water lost heat.

## Part 3. Calorimetry

7. Solid ammonium nitrate,  $\text{NH}_4\text{NO}_3$ , is dissolved in water in a coffee-cup calorimeter. The temperature of the water drops.

(a) What is the system? What are the surroundings?

System: **the dissolving  $\text{NH}_4\text{NO}_3$  (the reaction)**. Surroundings: **the water** (and the cup).

(b) Give the sign of  $q_{\text{soln}}$  and  $q_{\text{rxn}}$ . Is dissolving exothermic or endothermic?

The water lost heat, so  $q_{\text{soln}}$  is **negative** and  $q_{\text{rxn}}$  is **positive**. Dissolving is **endothermic**.

8. 10.0 g of  $\text{CaCl}_2$  (molar mass 110.98 g/mol) is dissolved in 90.0 g of water in a calorimeter. The temperature rises from 21.0 °C to 38.5 °C.

(a) Find  $q_{\text{soln}}$ . (Use the total mass of the solution.)

$$m = 10.0 \text{ g} + 90.0 \text{ g} = 100.0 \text{ g}; \Delta T = 17.5 \text{ }^\circ\text{C}. q_{\text{soln}} = (100.0 \text{ g})(4.18 \text{ J/g}\cdot^\circ\text{C})(17.5 \text{ }^\circ\text{C}) = \mathbf{7315 \text{ J (7.32 kJ)}}.$$

(b) Find  $q_{\text{rxn}}$ . Is dissolving  $\text{CaCl}_2$  exothermic or endothermic?

$$q_{\text{rxn}} = -q_{\text{soln}} = \mathbf{-7.32 \text{ kJ, exothermic}} \text{ (the water got warmer).}$$

(c) Find  $\Delta H$  in kJ/mol of  $\text{CaCl}_2$ .

$$\text{mol} = 10.0 \text{ g} \div 110.98 \text{ g/mol} = 0.09011 \text{ mol}. \Delta H = q_{\text{rxn}} \div \text{mol} = -7.315 \text{ kJ} \div 0.09011 \text{ mol} = \mathbf{-81.2 \text{ kJ/mol}}.$$

9. 150. g of water at 70.0 °C is mixed with 50.0 g of water at 10.0 °C in a calorimeter. Find the final temperature. (Heat lost = heat gained.)

$$-(150. \text{ g})(4.18)(T_f - 70.0) = (50.0 \text{ g})(4.18)(T_f - 10.0). \text{ Cancel c: } -150T_f + 10,500 = 50.0T_f - 500, \text{ so } 11,000 = 200.T_f \text{ and } T_f = \mathbf{55.0 \text{ }^\circ\text{C}}. \text{ It is closer to } 70 \text{ }^\circ\text{C} \text{ because there is more hot water.}$$

10. A student runs the  $\text{CaCl}_2$  experiment in a single foam cup with no lid. Some heat escapes into the air. Will the measured temperature rise be too high or too low? Will the calculated  $\Delta H$  be too large or too small in size? Explain.

The temperature rise will be **too low**, because some of the heat went into the air instead of the water. So  $q_{\text{soln}}$  and the calculated  $\Delta H$  will be **too small in size** (less negative than the true value). The lid and second cup are there to trap the heat.

## Part 4. Entropy, Enthalpy and Gibbs Energy

11. Predict the sign of  $\Delta S$  (+ or -) for each change and give a reason.

| Change                                                                                   | $\Delta S$ (+ or -) | Reason                                                       |
|------------------------------------------------------------------------------------------|---------------------|--------------------------------------------------------------|
| $\text{CO}_2(\text{s}) \rightarrow \text{CO}_2(\text{g})$                                | +                   | <i>solid <math>\rightarrow</math> gas</i>                    |
| $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{l})$ | -                   | <i>3 mol gas <math>\rightarrow</math> liquid (0 mol gas)</i> |
| $\text{NaCl}(\text{s}) \rightarrow \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq})$      | +                   | <i>dissolving a solid</i>                                    |
| $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$       | -                   | <i>3 mol gas <math>\rightarrow</math> 2 mol gas</i>          |
| $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{AgCl}(\text{s})$      | -                   | <i>forming a precipitate</i>                                 |

Gases have the most entropy, so counting moles of gas on each side usually decides the sign.

12. Calculate  $\Delta S^\circ$  for  $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$ . Does your answer match your prediction in the table above?

| Substance           | $\text{SO}_2(\text{g})$ | $\text{O}_2(\text{g})$ | $\text{SO}_3(\text{g})$ |
|---------------------|-------------------------|------------------------|-------------------------|
| $S^\circ$ (J/mol·K) | 248.2                   | 205.0                  | 256.8                   |

$$\Delta S^\circ = \sum nS^\circ_{\text{products}} - \sum nS^\circ_{\text{reactants}} = 2(256.8) - [2(248.2) + 205.0] = 513.6 - 701.4 = \mathbf{-187.8 \text{ J/K}}. \text{ Negative, which matches (3 mol gas } \rightarrow \text{ 2 mol gas).}$$

13. For the same reaction,  $\Delta H = -197.8 \text{ kJ}$  and  $\Delta S = -187.8 \text{ J/K}$ .

(a) Calculate  $\Delta G$  at 25 °C. Is the reaction spontaneous?

$$T = 298 \text{ K}; \Delta S = -0.1878 \text{ kJ/K}. T\Delta S = (298 \text{ K})(-0.1878 \text{ kJ/K}) = -56.0 \text{ kJ}. \Delta G = -197.8 \text{ kJ} - (-56.0 \text{ kJ}) = \mathbf{-141.8 \text{ kJ}}. \Delta G < 0, \text{ so it is } \mathbf{\text{spontaneous}}.$$

(b) Above what temperature does this reaction stop being spontaneous?

$$\Delta G = 0 \text{ when } T = \Delta H \div \Delta S = (-197.8 \text{ kJ}) \div (-0.1878 \text{ kJ/K}) = \mathbf{1.05 \times 10^3 \text{ K}}. \text{ Both signs are negative, so it is spontaneous only at low temperature.}$$

14. Complete the table for the four combinations of  $\Delta H$  and  $\Delta S$ .

| $\Delta H$ | $\Delta S$ | Is the reaction spontaneous?                                  |
|------------|------------|---------------------------------------------------------------|
| –          | +          | <i>always, at any temperature</i>                             |
| –          | –          | <i>only at low temperature (<math>\Delta H</math> wins)</i>   |
| +          | +          | <i>only at high temperature (<math>T\Delta S</math> wins)</i> |
| +          | –          | <i>never, at any temperature</i>                              |

Use  $\Delta G = \Delta H - T\Delta S$ . When the two signs disagree, temperature decides.

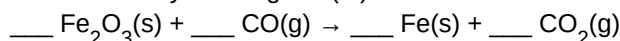
## Part 5. Heat of Formation Calculations

15. Circle every substance whose  $\Delta H_f^\circ$  is zero. Explain why the others are not zero.

$O_2(g)$   $H_2O(l)$   $Fe(s)$   $O_3(g)$   $N_2(g)$   $Br_2(l)$   $Br_2(g)$   $NaCl(s)$   $C(s, \text{graphite})$

Zero:  **$O_2(g)$ ,  $Fe(s)$ ,  $N_2(g)$ ,  $Br_2(l)$ ,  $C(s, \text{graphite})$** , elements in their standard states.  $H_2O$  and  $NaCl$  are compounds,  $O_3$  is not oxygen's standard form, and  $Br_2(g)$  is not bromine's standard state (liquid).

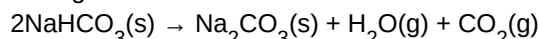
16. Iron is made by reacting iron(III) oxide with carbon monoxide. Balance the equation, then calculate  $\Delta H_{rxn}^\circ$ .



| Substance                   | $Fe_2O_3(s)$ | $CO(g)$ | $Fe(s)$ | $CO_2(g)$ |
|-----------------------------|--------------|---------|---------|-----------|
| $\Delta H_f^\circ$ (kJ/mol) | –824.2       | –110.5  | 0       | –393.5    |

Balanced:  $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$ . Products:  $2(0) + 3(-393.5) = -1180.5$  kJ. Reactants:  $-824.2 + 3(-110.5) = -1155.7$  kJ.  
 $\Delta H_{rxn}^\circ = (-1180.5) - (-1155.7) = \mathbf{-24.8 \text{ kJ}}$ , exothermic.

17. Baking soda breaks down when heated in an oven. Calculate  $\Delta H_{rxn}^\circ$  and explain why the oven must keep supplying heat.

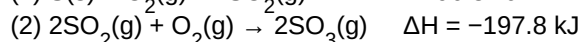
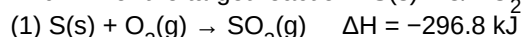


| Substance                   | $NaHCO_3(s)$ | $Na_2CO_3(s)$ | $H_2O(g)$ | $CO_2(g)$ |
|-----------------------------|--------------|---------------|-----------|-----------|
| $\Delta H_f^\circ$ (kJ/mol) | –950.8       | –1130.7       | –241.8    | –393.5    |

Products:  $-1130.7 + (-241.8) + (-393.5) = -1766.0$  kJ. Reactants:  $2(-950.8) = -1901.6$  kJ.  $\Delta H_{rxn}^\circ = (-1766.0) - (-1901.6) = \mathbf{+135.6 \text{ kJ}}$ . It is **endothermic**, so it absorbs heat and only continues while heat is supplied. (Use  $H_2O(g)$ , not  $H_2O(l)$ .)

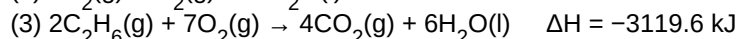
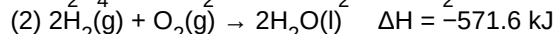
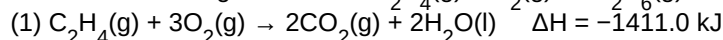
## Part 6. Hess's Law

18. Find  $\Delta H$  for the target reaction:  $S(s) + 3/2 O_2(g) \rightarrow SO_3(g)$



Keep (1):  $-296.8$  kJ. Multiply (2) by  $1/2$ :  $SO_2 + 1/2 O_2 \rightarrow SO_3$ ,  $\Delta H = -98.9$  kJ. Add:  $SO_2$  cancels and  $O_2$  adds to  $3/2 O_2$ .  $\Delta H = -296.8 + (-98.9) = \mathbf{-395.7 \text{ kJ}}$ .

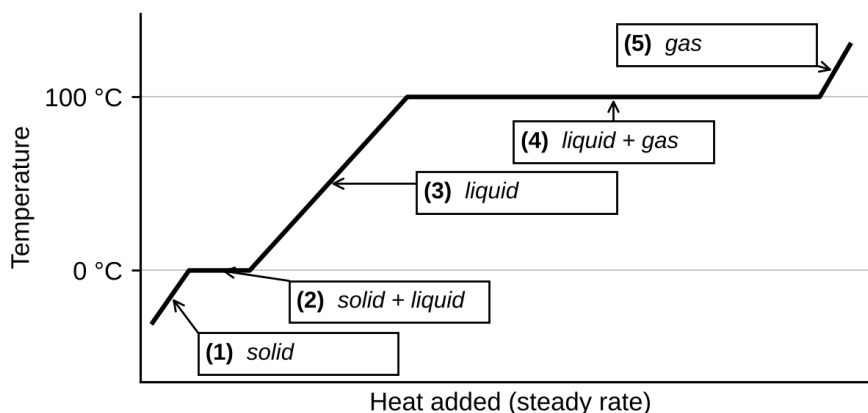
19. Find  $\Delta H$  for the target reaction:  $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$



Keep (1):  $-1411.0$  kJ. Multiply (2) by  $1/2$ :  $H_2 + 1/2 O_2 \rightarrow H_2O$ ,  $-285.8$  kJ. Reverse (3) and multiply by  $1/2$ :  $2CO_2 + 3H_2O \rightarrow C_2H_6 + 7/2 O_2$ ,  $+1559.8$  kJ.  $O_2$  ( $7/2$  each side),  $2CO_2$ , and  $3H_2O$  cancel.  $\Delta H = -1411.0 - 285.8 + 1559.8 = \mathbf{-137.0 \text{ kJ}}$ .

## Part 7. Heating and Cooling Curves

20. Ice is heated at a steady rate. In each box, write the phase or phases present. Write the melting and boiling temperatures on the blanks.



| Segment       | Does KE or PE increase?   | Equation for q                         |
|---------------|---------------------------|----------------------------------------|
| (1), (3), (5) | KE (temperature rises)    | $q = mc\Delta T$ ( $c$ for that phase) |
| (2)           | PE (temperature constant) | $q = m\Delta H_{fus}$                  |
| (4)           | PE (temperature constant) | $q = m\Delta H_{vap}$                  |

(a) On segment (4), heat is still being added, but the temperature does not change. Where does the energy go?

It goes into **potential energy**, pulling the particles apart into a gas. The temperature (average KE) stays the same.

(b) Why is plateau (4) much longer than plateau (2)?

Boiling takes about 7 times more heat than melting ( $\Delta H_{vap} = 2260 \text{ J/g}$  vs.  $\Delta H_{fus} = 334 \text{ J/g}$ ). Boiling pulls the particles completely apart; melting only loosens them.

Sloped segments have one phase and a changing temperature. Flat segments are phase changes with two phases present.

21. How much heat is needed to change 20.0 g of water at 25.0 °C into steam at 110.0 °C? Show one q for each segment.

$q_1$  (warm water) =  $(20.0)(4.18)(75.0) = 6270 \text{ J}$ .  $q_2$  (boil) =  $(20.0 \text{ g})(2260 \text{ J/g}) = 45,200 \text{ J}$ .  $q_3$  (warm steam) =  $(20.0)(1.99)(10.0) = 398 \text{ J}$ .  $q_{\text{total}} = 51,868 \text{ J} = 5.19 \times 10^4 \text{ J (51.9 kJ)}$ .