

Experiment

9

Thermochemistry: Determination of the Heat of Neutralization

INTRODUCTION

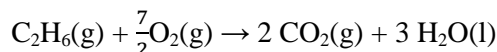
A chemical reaction is often accompanied by a heat change. Thermochemistry deals with the experimental measurement and calculation of such heat changes. The heat change that accompanies the reaction of one mole of substance is designated by the symbol Q . In an exothermic reaction, heat is evolved, and Q , by convention, is a negative quantity. If heat is absorbed, the reaction is endothermic and Q is a positive quantity. Heat changes for chemical reactions are usually given in calories or joules. A calorie is the quantity of heat required to raise the temperature of one gram of water one degree centigrade and one calorie equals 4.18 joules.

When the heat change for a reaction is measured under conditions of constant pressure, as is the case with most chemical reactions open to the atmosphere, it equals a state function of the system called the enthalpy change, ΔH

$$Q_p = \Delta H \quad (1)$$

Since $\Delta H = Q_p$, a negative value for ΔH indicates an exothermic reaction and a positive value of ΔH indicates an endothermic reaction.

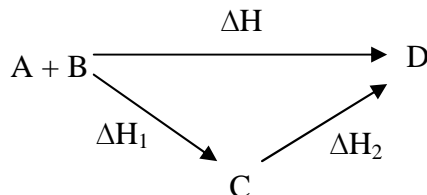
Whenever ΔH for a reaction is given, both the quantity of material reacting and the states of matter involved in the reaction (s, l, g) must be clearly specified. For example, when one mole of ethane is oxidized



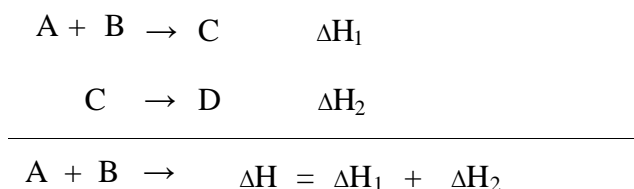
$\Delta H = -1559\text{kJ}$. If two moles of C_2H_6 were oxidized, twice as much heat would be liberated, and if $\text{H}_2\text{O}(\text{g})$ rather than $\text{H}_2\text{O}(\text{l})$ were the product, less heat would be liberated since heat is required to change $\text{H}_2\text{O}(\text{l})$ to $\text{H}_2\text{O}(\text{g})$.

State functions, such as enthalpy changes, are important in chemistry because their values are constant for a given chemical or physical change. The change in the value of a state function depends only on the initial and final states of the system, and not on the path used to bring about the change. This property allows ΔH or any other state function, to be determined for reactions for which there is no direct experimental data.

For example, suppose ΔH for the reaction $\text{A} + \text{B} \rightarrow \text{D}$ is unknown and cannot be measured directly. By using the fact that the enthalpy change for a reaction is independent of path, ΔH for this reaction can be calculated if other reactions with known values of ΔH can be arranged to form an alternate path from the initial state, $\text{A} + \text{B}$, to the final state, D . The process is illustrated in the following diagram.



Since the enthalpy change is independent of path, ΔH for the reaction must equal $\Delta H_1 + \Delta H_2$. This is equivalent to algebraically combining the known values of ΔH in the same manner as the reactions to which they correspond. If a reaction is reversed, the sign of ΔH is changed.



In this experiment, ΔH for three acid-base neutralization reactions are determined by direct measurement. First, the neutralization of a strong acid, HCl, by a strong base, NaOH, is studied. The heat change for this reaction corresponds to the net ionic equation



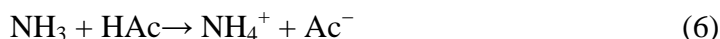
Second, ΔH for the neutralization of a weak acid, HAc, by a strong base, NaOH, is measured. The corresponding net ionic equation is



Third, ΔH for the neutralization of a weak base, NH_3 , by a strong acid, HCl, is measured. The corresponding net ionic equation is



Finally, ΔH for the reaction of a weak base, NH_3 , with a weak acid, HAc, is calculated using the thermochemical data obtained for reactions (3), (4), and (5) and the fact that ΔH is a state function. The net ionic equation for this reaction is



The heat change that accompanies a chemical or physical process is usually determined experimentally by measuring the temperature changes that occur when the process is conducted in a well-insulated container called a calorimeter. Ideally, a calorimeter does not allow heat to be absorbed from or escape to the surroundings. Any heat change is confined to the calorimeter and its contents. In an exothermic process the heat evolved by the process is gained by the calorimeter and its contents. In an endothermic process the heat absorbed by the process is lost by the calorimeter and its contents.

In neutralization reactions, acid and base solutions are mixed in a calorimeter. The heat evolved by the reaction of the acid and base is absorbed by the calorimeter and the solution formed on mixing the acid and base.

$$\begin{array}{l} \text{heat evolved by} \\ \text{the reaction} \end{array} = \begin{array}{l} \text{heat absorbed by} \\ \text{the calorimeter} \end{array} + \begin{array}{l} \text{heat absorbed} \\ \text{by the solution} \end{array} \quad (7)$$

The total heat evolved by the reaction is designated by the symbol q . The heat absorbed by the calorimeter in this experiment is very small and will be neglected.

The heat absorbed by the solution is proportional to the mass and temperature change, ΔT , of the solution.

$$\text{heat absorbed by the solution} = c_{\text{soln}} \cdot m_{\text{soln}} \cdot \Delta T \quad (8)$$

The proportionality constant, c_{soln} , is the specific heat of the solution. Specific heat is defined as the number of joules required to raise the temperature of one gram of a substance one degree centigrade. Neglecting the heat absorbed by the calorimeter, equation (7) can be rewritten as

$$q = c_{\text{soln}} \cdot m_{\text{soln}} \cdot \Delta T \quad (9)$$

In the acid-base neutralization reactions studied in this experiment, the solutions in the calorimeter are mainly water, since the acid and base solutions are dilute. Thus, the specific heat of water, $4.18 \text{ J/g } ^\circ\text{C}$, can be used for c_{soln} , and m_{soln} can be calculated from the total volume of solution used and the known density of water, $D = 1.0 \text{ g/cm}^3$. ΔT is measured directly.

The number of joules absorbed or released per mole of reactant is calculated by dividing the heat change, q , by the number of moles of **either acid or base** used, n .

$$Q = -\frac{q}{n} \quad (10)$$

The negative sign is inserted here since Q by convention is negative for an exothermic reaction. Finally, $Q = \Delta H$ since the reaction occurs at constant pressure.

$$\Delta H = -\frac{q}{n} \quad (11)$$

The enthalpy of neutralization is calculated using equations (9) and (11) and the experimental data for ΔT and n . ΔT for the neutralization is obtained by measuring the temperatures of the acid and base before mixing and the temperature of the mixture after mixing. The temperatures are recorded at known time intervals. The values are plotted on a temperature versus time graph and the best straight line for each set of data is extrapolated to the time of mixing. Typical results are illustrated in Figure 9-1. Note that the acid and base are at the same initial temperature.

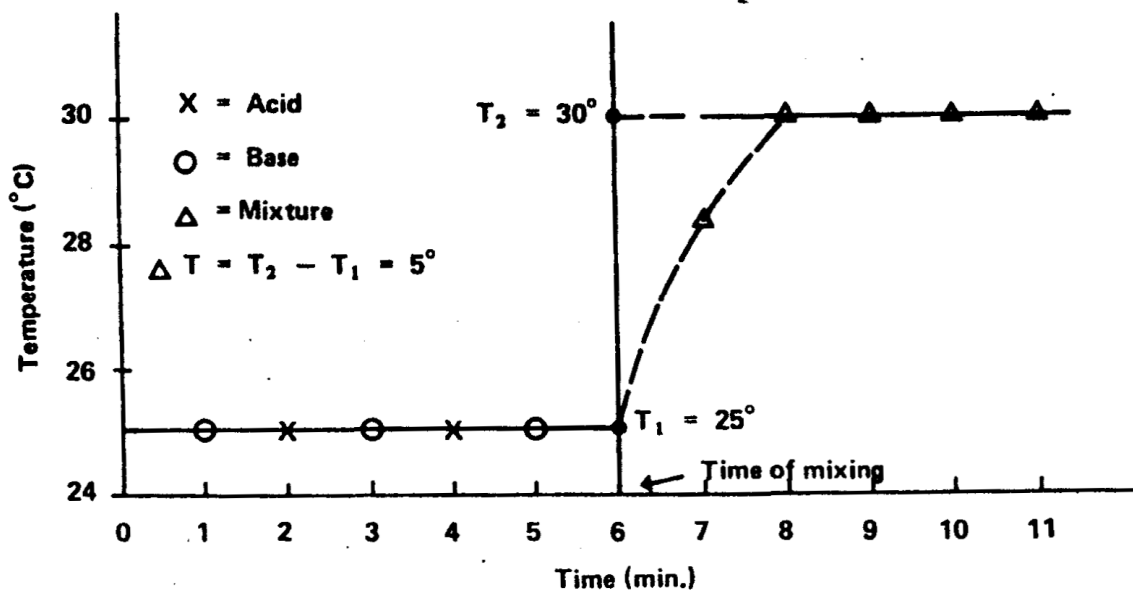


Figure 9-1. Plot of temperature-time data for the determination of the enthalpy of neutralization.

PROCEDURE

1. Obtain a thermometer calibrated to 0.1 °C and a calorimeter from the stockroom. The calorimeter consists of two styrofoam cups, one placed inside the other, and a large cork in which the thermometer can be inserted. The thermometers are expensive and should be used with care.

Determination of Heat of Neutralization

2. Measure 50mL of 1.0M NaOH in a graduated cylinder and add the base to the calorimeter. Rinse the graduated cylinder several times with water and once with 5mL of 1.0M HCl. Measure 50mL of the 1.0M HCl in the graduated cylinder and add it to a 250mL beaker.
3. Record the temperature of the acid and base solutions to ± 0.1 °C at 60-second intervals until at least three readings for each solution have been taken. The temperatures of the two solutions should be the same. If they are not, see your instructor. Rinse and dry the thermometer between each reading. Add the solution in the beaker to the calorimeter, and mix thoroughly by swirling the contents. Record the temperature of the mixture to ± 0.1 °C at 30-second intervals for at least 3 minutes.
4. Plot all the data on one temperature-time graph and draw smooth lines through the data for the acid, the base, and the mixture as shown in Figure 9-1. Since the acid and base were at the same temperature, these lines should coincide. Extrapolate the lines to the time of mixing. Record the temperature of the acid and base solution (T_1) and the mixture (T_2) at the time of mixing. Calculate the ΔT , q , n , and the enthalpy of neutralization. Refer to Equations 9 and 11, and the information on the top of the preceding page to carry out these calculations.
5. Repeat steps 2, 3, and 4 for 1.0 M NaOH and 1.0 M HAc.
6. Repeat steps 2, 3, and 4 for 1.0 M NH_3 and 1.0 M HCl.
7. Calculate ΔH for the reaction of 1.0 M NH_3 with 1.0M HAc using the enthalpy of neutralization data determined in this experiment.

THERMOCHEMISTRY:
DETERMINATION OF THE HEAT OF NEUTRALIZATION

Name _____

Section _____

DATA AND RESULTS
Determination of Heat of Neutralization

1M NaOH + 1M HCl

Volume of NaOH _____

Volume of HCl _____

Total volume after mixing _____

Time (min)	Temperature (°C)		
	NaOH	HCl	Mixture
0.0			
1.0			
2.0			
3.0			
4.0			
5.0			
6.0			
6.5			
7.0			
7.5			
8.0			
8.5			

net ionic equation _____

$T_1 =$

$T_2 =$

$\Delta T = T_2 - T_1 =$

$q =$

$n =$

$\Delta H =$

Calculation

1M NaOH + 1M HAc

Volume of NaOH _____

Volume of HAc _____

Total volume after mixing _____

Time (min)	Temperature (°C)		
	NaOH	HAc	Mixture
0.0			
1.0			
2.0			
3.0			
4.0			
5.0			
6.0			
6.5			
7.0			
7.5			
8.0			
8.5			

net ionic equation _____

$T_1 =$ _____

$T_2 =$ _____

$\Delta T = T_2 - T_1 =$ _____

$q =$ _____

$n =$ _____

$\Delta H =$ _____

Calculation

1M NH₃ + 1M HCl

Volume of NH₃

Volume of HCl

Total volume after mixing

Time (min)	Temperature (°C)		
	NH ₃	HCl	Mixture
0.0			
1.0			
2.0			
3.0			
4.0			
5.0			
6.0			
6.5			
7.0			
7.5			
8.0			
8.5			

net ionic equation _____

T₁ = _____

T₂ = _____

ΔT = T₂ - T₁ = _____

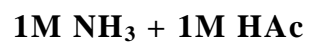
q = _____

n = _____

ΔH = _____

Calculation

Determination of the Heat of Neutralization Using Hess' Law



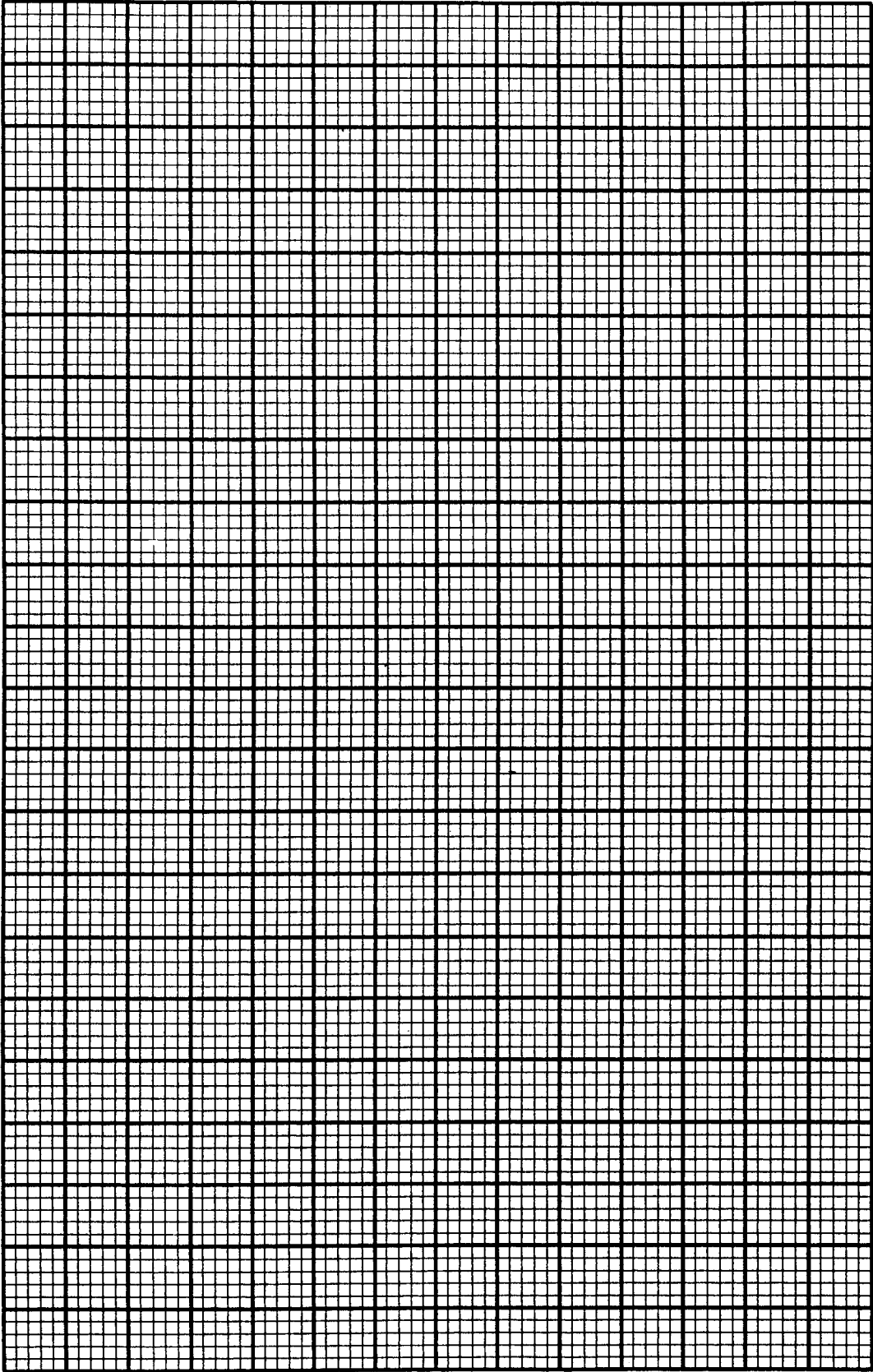
net ionic equation _____

$\Delta H =$ _____

Calculation: (Show all work!)

Temperature (°C)

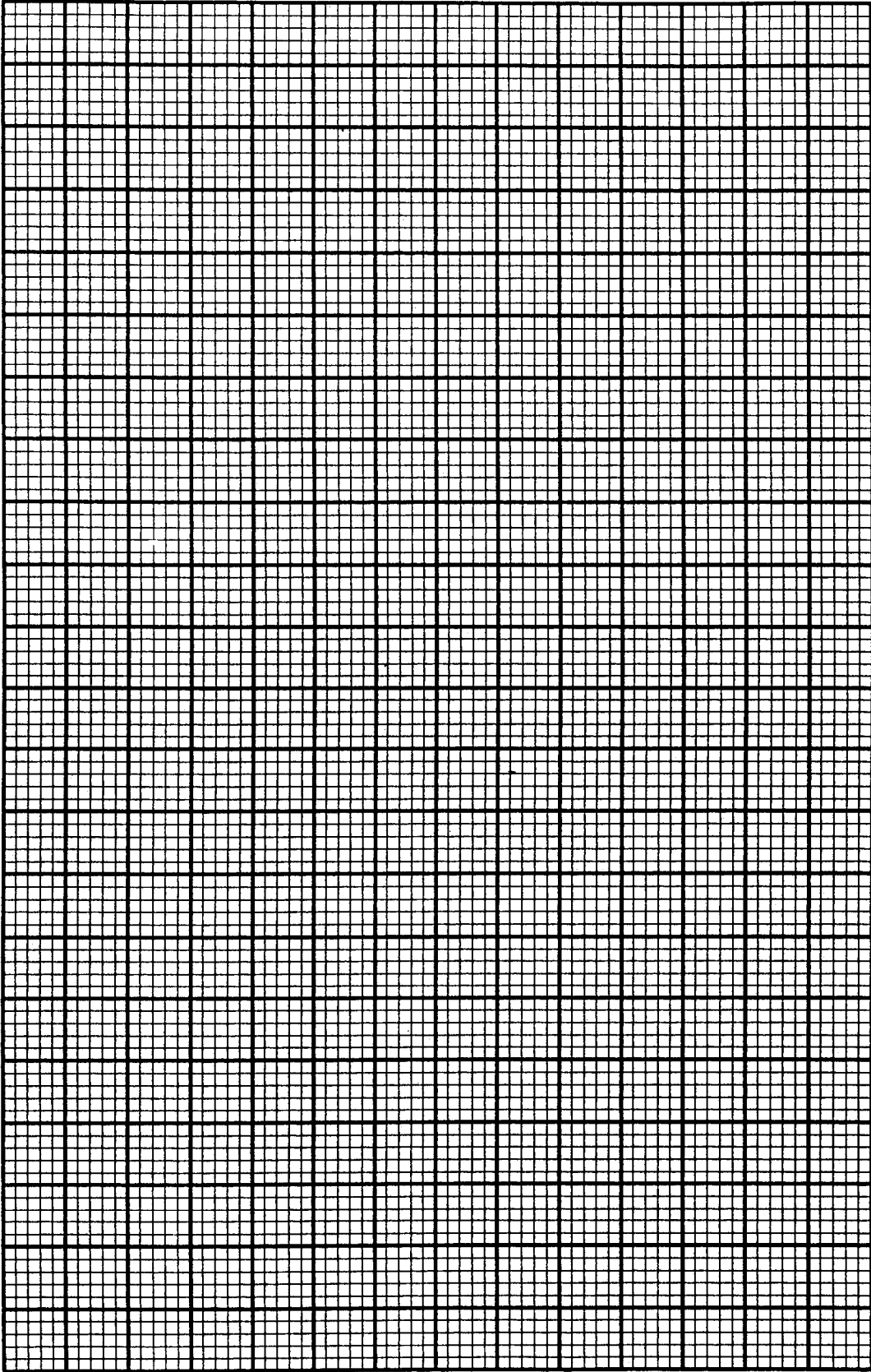
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Time (minutes)

Temperature (°C)

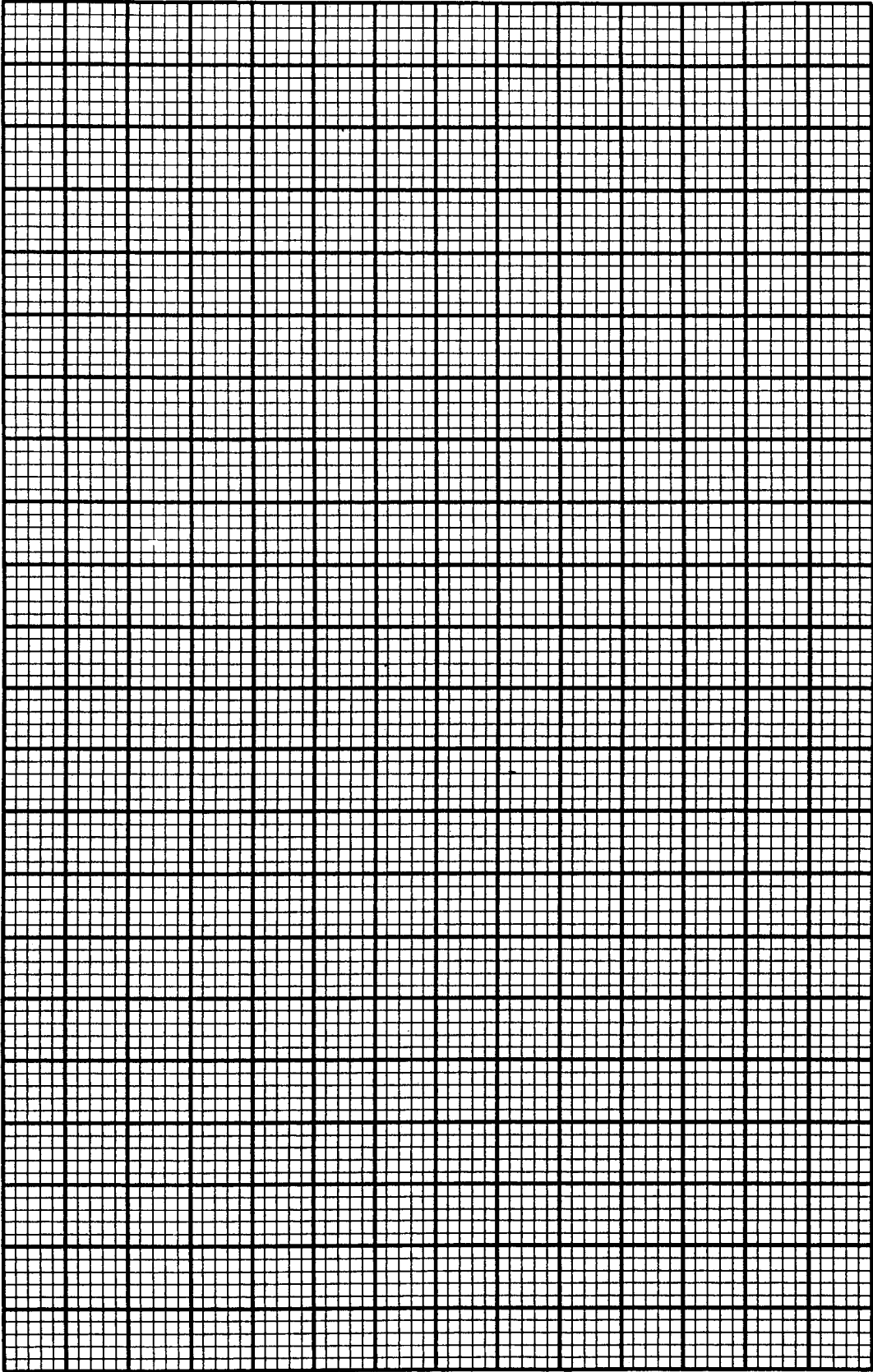
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Time (minutes)

Temperature (°C)

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Time (minutes)