EXPERIMENT

Entropy and spontaneity

Goal

The goal of this laboratory experiment is to calculate the minimum entropy change for a chemical reaction involving the dissolution of sodium nitrate.

Materials

☐ A coffee-cup calorimeter   ☐ $NaNO_3(s)$

☐ A thermometer and a lit for the calorimeter

Background

Standard molar entropy

The standard molar entropy of a substance is the absolute entropy of one more substance at 1 atm. Entropies are absolute properties in contrast to other relative thermodynamic functions like the enthalpy in which a set of molecular states act as a reference. The tabulated standard entropy values are listed at the end of the chapter at one bar and 25 °C, the conventional temperature for reporting thermodynamic data. The units of molar entropy are J/molK. Molar entropies tend to be small values–as the unit joule is a small unit of energy. Finally, entropies can be positive or negative values.

Factors affecting entropy

We can qualitatively rationalize the trends between the standard molar entropy values for different substances and different conditions (temperature, volume, pressure) by using some simple rules described below:

⚐ **The state of matter:** The standard entropy of gases is larger than the standard entropy of liquids as gases present a larger degree of freedom (possible configurations) than liquids. The standard entropy of liquids is larger than the standard entropy of solids as liquids present a large degree of freedom than solids. The molecules of a liquid molecules can jiggle more in comparison with the molecules of a solid. Overall, we can assume that liquids and solid has almost null entropy whereas gases have very large entropy. For example, the entropies of ice, water, and steam are respectively 41, 69.95, and 69.95 J/molK.

⚐ **Molar mass:** For monoatomic substances (e.g. Ne, Ar, etc.) the larger the atomic weight the larger entropy. This is because the energy levels of larger molecules are more packed, and hence are easier to access at a given temperature.

⚐ **Molecular complexity:** For substances with comparable molar mass (O_3 and F_2), the more complex the molecule the larger entropy, as the number of degrees of freedom is directly correlated with the number of microstates.

⚐ **Temperature:** Temperature increases entropy as the system has more accessible microstates. The plot below represents the entropy change with temperature for a substance.

⚐ **Number of particles:** The larger the number of particles of a system, the larger the entropy, as the more particles the more microstates or possible configurations.

⚐ **Volume:** The larger the volume of a system, the larger the entropy, as the larger volume the more microstates of possible configurations.

Calculating entropy changes in reactions

We can calculate the standard entropy of a reaction in a similar way as we calculate the standard enthalpy of a reaction:

$$\boxed{\Delta S_R^\circ = \Delta S_{products}^\circ - \Delta S_{reactants}^\circ}$$ Entropy change   (1)
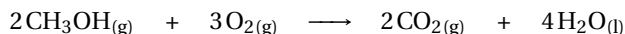
where:

ΔS_R° is the standard entropy change of the reaction

$\Delta S_{products}^\circ$ is the standard entropy of all products

$\Delta S_{reactants}^\circ$ is the standard entropy of all reactants

It is important to take into account the stoichiometric coefficients. For example, for the reaction:

$$2\,CH_3OH_{(g)} \quad + \quad 3\,O_{2\,(g)} \quad \longrightarrow \quad 2\,CO_{2\,(g)} \quad + \quad 4\,H_2O_{(l)}$$

We have the entropy values of: $S^\circ(CH_3OH_{(g)})$=239.7 J/K· mol, $S^\circ(O_{2\,(g)})$=161.1 J/K· mol, $S^\circ(CO_{2\,(g)})$=213.79 J/K· mol, and $S^\circ(H_2O_{(l)})$=69.95 J/K· mol. We can calculate ΔS_R°:

$$\Delta S_R^\circ = \Delta S_{products}^\circ - \Delta S_{reactants}^\circ =$$
$$\left(2 \cdot S^\circ(CO_{2\,(g)}) + 4 \cdot S^\circ(H_2O_{(l)})\right) - \left(2 \cdot S^\circ(CH_3OH_{(g)}) + 3 \cdot S^\circ(O_{2\,(g)})\right)$$
$$= \left(2 \cdot 213.79 + 4 \cdot 69.95\right) - \left(2 \cdot 239.7 + 3 \cdot 161.1\right) = -255.32\,J/K$$

Estimating the sign of the entropy changes in reactions

Oftentimes times were are more interested in predicting the sign of the entropy change of a reaction than in computing the exact value. This is because the sign can be used to estimate whether a reaction proceeds spontaneously. Two basic rules are used to estimate the entry change sign:

The state of matter: solids and liquids have very low entropy in comparison to gases. For example, in the case below, we have the production of liquid water from ice produces entropy as liquids have more entropy than solids:

$H_2O_{(s)} \longrightarrow H_2O_{(l)}$ $\hfill \Delta S_R^\circ > 0$

On the other hand, the condensation of water vapor to produce a liquid consumes entropy, as liquids have less entropy than gases:

$H_2O_{(g)} \longrightarrow H_2O_{(l)}$ $\hfill \Delta S_R^\circ < 0$

The number of molecules: the larger the number of molecules of gas the larger entropy. For example, in the reaction below we have that we produce three molecules from two molecules. Hence, the entropy increases.

$2\,SO_{3\,(g)} \longrightarrow 2\,SO_{2\,(g)} + O_{2\,(g)}$ $\hfill \Delta S_R^\circ < 0$

However, this rule only works if we only take into account the number of gas molecules. For example, in the reaction below we produce two gas molecules from three gas molecules and hence we lose entropy:

$2\,H_2S_{(g)} + SO_{2\,(g)} \longrightarrow 3\,S_{(s)} + 2\,H_2O_{(g)}$ $\hfill \Delta S_R^\circ < 0$

Gibbs free energy

The Gibbs free energy is just a combination of enthalpy and entropy for a given temperature:

$$G = H - T \cdot S \tag{2}$$

Working at constant temperature, we can compute the change in Gibbs free energy as:

$$\boxed{\Delta G^T = \Delta H - T\Delta S \quad \text{Gibbs free-energy}} \tag{3}$$

where:

ΔG^T is the Gibbs free-energy change at constant temperature

ΔH is the enthalpy change

ΔS is the entropy change

T is the temperature

Gibbs free energy is a state function that only depends on the final and initial state and not the path followed. At the same time, Gibbs free energy depends on temperature and pressure–we will discuss more about this at the end of the section. More importantly, the change in Gibbs free energy is associated with the spontaneity of the process. Gibbs free-energy decreases with temperature and the decrease is sharper for gases in comparison to liquids, and at the same time, the decrease is also sharper for liquids in comparison to solids.

Gibbs free energy and spontaneity

The Gibbs free-energy change of a reaction is associated with the spontaneity of the process or with its state of equilibrium. In particular, reactions that produce Gibbs free energy are nonspontaneous. Differently, reactions consuming free energy are indeed spontaneous. Finally, reactions without a change in free energy are in equilibrium.

- ℣ $\Delta G < 0$**:** The reaction is spontaneous

- ℣ $\Delta G = 0$**:** The reaction is in equilibrium

- ℣ $\Delta G > 0$**:** The reaction is nonspontaneous

This is because the expression of Gibbs free energy is related to the total entropy change of the universe given by the second law of thermodynamics:

$$\Delta G^T = \Delta H - T\Delta S \quad \text{and} \quad T\Delta S_{univ}^{T,P} = -(\Delta H - T\Delta S) \tag{4}$$

Hence, we have that

$$\Delta G^T = T\Delta S_{univ}^{T,P} \tag{5}$$

This last expression means that an increase in total entropy is accompanied by a decrease in Gibbs free energy at constant pressure and temperature. At the same time, the expression indicates that the direction of spontaneous change corresponds to a decrease of Gibbs free energy, at constant temperature and pressure.

How to find extrapolated temperature

A calorimeter is ideally an isolated system. That means the heat produced does not leave the cup. If a reaction is exothermic–if it produces heat–the temperature inside the calorimeter will increase. Differently, for an endothermic reaction–a reaction that consumes heat–the temperature inside the calorimeter will decrease. When the reaction stops, as there is no more heat being produced or consumed, the temperature inside the calorimeter will change. To estimate the temperature at that point, we need to extrapolate the temperature inside the calorimeter. If you plot temperature versus time you will see that for early times, the temperature inside a calorimeter in which a reaction happens changes abruptly. After that, the temperature slowly decreases with time. To calculate the temperature when the reaction stops you need to connect the dots of the later stages, when the reaction already has stopped. We call this interpolation. All these points will be part of a line. If you extend the line, it will cross the Y-axis, and that crossing point is the temperature at which the reaction has stopped. We call this the extrapolation method.

Example

The following data reports the temperature inside a cup calorimeter. Indicate whether the reaction is exothermic or endothermic and calculate the temperature when the reaction stops employing the extrapolation method.

t (min)	0	1	2	3	4	5	6	7	8	9	10
T (°C)	10	10	20	28	29	30	29.5	29	28.5	27.5	27

Answer: if we plot temperature versus time we will see the two different regions of the plot. In early times, the temperature increased and hence the reaction in the calorimeter was exothermic. At later times, the reaction stops and temperature decreases due to the lack of heat release. We will use the last points and connect them with a line. The crossing point with the Y axis is 33 °C and that is the final temperature of the reaction.
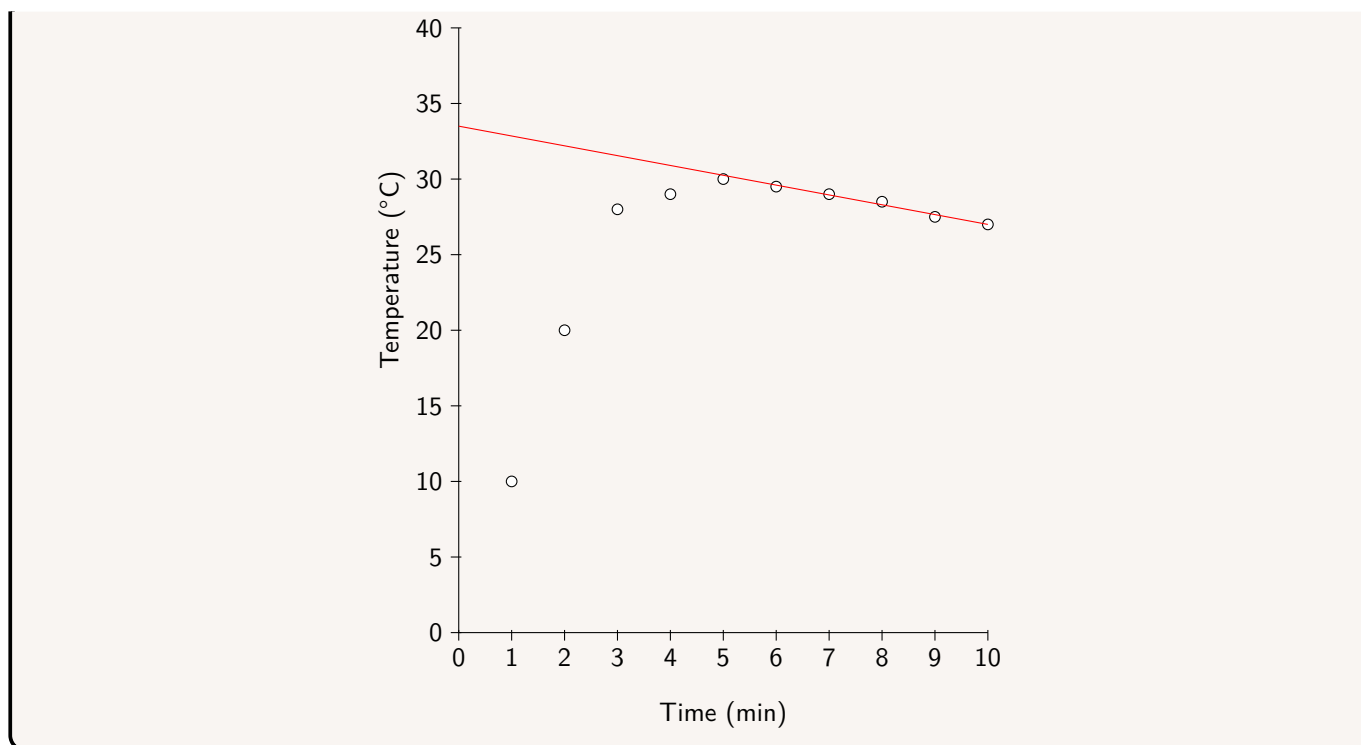
Procedure

☐ *Step 1:* – Obtain a coffee cup calorimeter with a thermometer and a plastic lid.

☐ *Step 2:* – Weight about 8.5g of $NaNO_3$. Write down the mass you weighed in the results section.

☐ *Step 3:* – Use a 100mL graduated cylinder to add 100mL of distilled water in the calorimeter.

☐ *Step 4:* – Measure the temperature of water in the calorimeter. Record this temperatures as your initial temperature t_i.

☐ *Step 5:* – Get the timer ready. Time should be taken as soon as the solid reactant is added.

☐ *Step 6:* – Add the $NaNO_3$ to the calorimeter. If you are using a magnetic stirrer set the speed to a medium speed and make sure the heating option is off. Then add the solid. Start the timer immediately and place the lid on the calorimeter.

☐ *Step 7:* – Record the temperature for 4 min. Do not stop the timer during the experiment. Record the results in the results table.

☐ *Step 8:* – Replicate the experiment one more time.

☐ *Step 9:* – Plot the temperature of the calorimeter against time and use a straight line to extrapolate your results against the starting time (time = 0 s). Plot the results for both replicates in the same plot. Record the extrapolated temperature as t_f.

☐ *Step 10:* – Do not carry out any calculation before finishing the plot from the previous step. Calculate the change of enthalpy, ΔH.

☐ *Step 11:* – Calculate the average enthalpy change using the two replicated experiments.

☐ *Step 12:* – If your instructor assigns you an unknown solute, repeat the previous procedure with this new solute.

Calculations

① This is the initial temperature before you add the solid.

② This is the final temperature after the dissolution reaction stops. You need to plot the data and extrapolate to get this value.

③ This is the maximum temperature during the experiment. Comparing the initial and final temperatures you can figure out of the reaction is endothermic or exothermic.

④ This is the mass of salt weighed.

⑤ This is the number of moles of salt:

$$④ / \ 84.9947$$

⑥ You can calculate the enthalpy change (ΔH in KJ/mol) by means of the following formula:

$$\Delta H = -\frac{1 \times 10^{-3}}{⑤} \cdot \left(4.184 \cdot 1.0 \cdot 100.0 \cdot (② - ①) + 10 \cdot (② - ①)\right)$$

⑦ This is the average enthalpy.

⑧ This is the average maximum temperature.

⑨ Calculate the minimum entropy change for equilibrium using the maximum temperature and the average enthalpy (remember enthalpy is expressed in KJ/mol and entropy in J/molK)

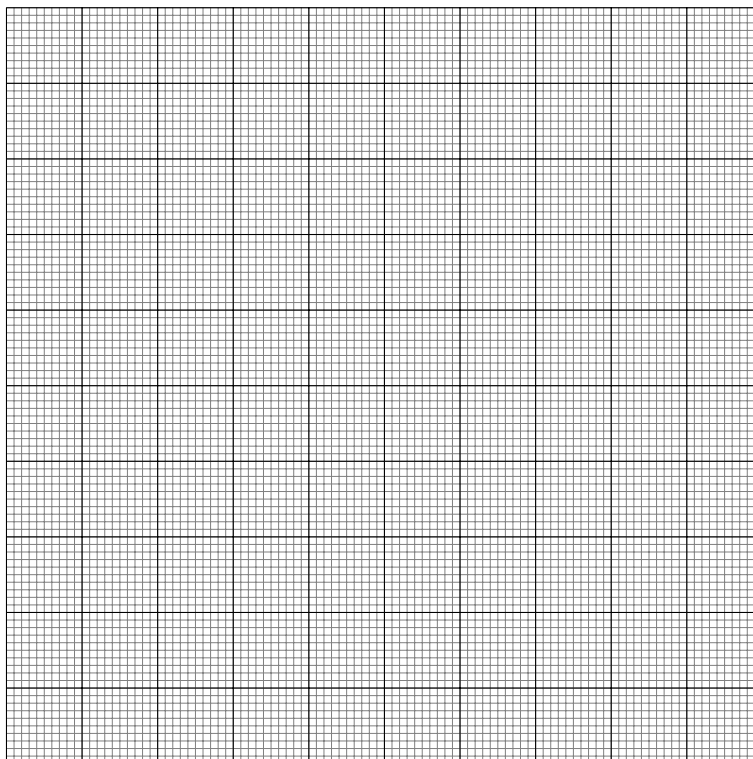$$\Delta S_{min} = \frac{\Delta H}{T_m} = \frac{⑦ \times 1000}{⑧}$$

Pre-lab Questions

Entropy and spontaneity

1. Ammonium nitrate (NH_4NO_3) is dissolved in a coffee-cup calorimeter. We recorded the temperatures with time and the data is given below. The initial temperature, t_i was 25.0 °C.

t (s)	0	30	60	90	120	150	180	210	240
T (°C)	25	40.8	40.7	40.6	40.5	40.4	40.3	40.2	40.1

(a) Plot T (vertical axis) vs. t (horizontal axis).

(b) Obtain t_f, the final temperature after the reaction starts, by extrapolating to the time of mixing (time = 0 s) with a straight line.

(c) Indicate whether this is an exothermic or an endothermic reaction.

(d) Explain the change of temperature inside the calorimeter.

2. Predict the sign of the entropy change for the dissolution of NH_4NO_3.

3. Predict the spontaneity of the dissolution of NH_4NO_3 using the signs of the entropy and enthalpy estimated above.

4. Calculate the $NaNO_3$ (MW=84.9947 $g \cdot mol^{-1}$) mass needed to prepare 100mL of a 1M solution of this salt.

STUDENT INFO

Name:

Date:

Entropy and spontaneity

NaNO$_3$ Trial 1

t (s)	0	30	60	90	120	150	180	210	240
T (°C)									

	T_i (°C)	T_f (°C)	T_m (°C)	m (g)	n (moles)	$\Delta H(kJ/mol)$
	①	②	③	④	⑤	⑥

NaNO$_3$ Trial 2

t (s)	0	30	60	90	120	150	180	210	240
T (°C)									

	T_i (°C)	T_f (°C)	T_m (°C)	m (g)	n (moles)	$\Delta H(kJ/mol)$

Average ΔH (kJ/mol) = ⑦

Average T_m (K) = ⑧

ΔS_{min} $(J/molK)$ = ⑨

Unknown Trial 1

t (s)	0	30	60	90	120	150	180	210	240
T (°C)									

T_i (°C)	T_f (°C)	T_m (°C)	m (g)	n (moles)	ΔH (kJ/mol)
①	②	③	④	⑤	⑥

Unknown Trial 2

t (s)	0	30	60	90	120	150	180	210	240
T (°C)									

T_i (°C)	T_f (°C)	T_m (°C)	m (g)	n (moles)	ΔH (kJ/mol)

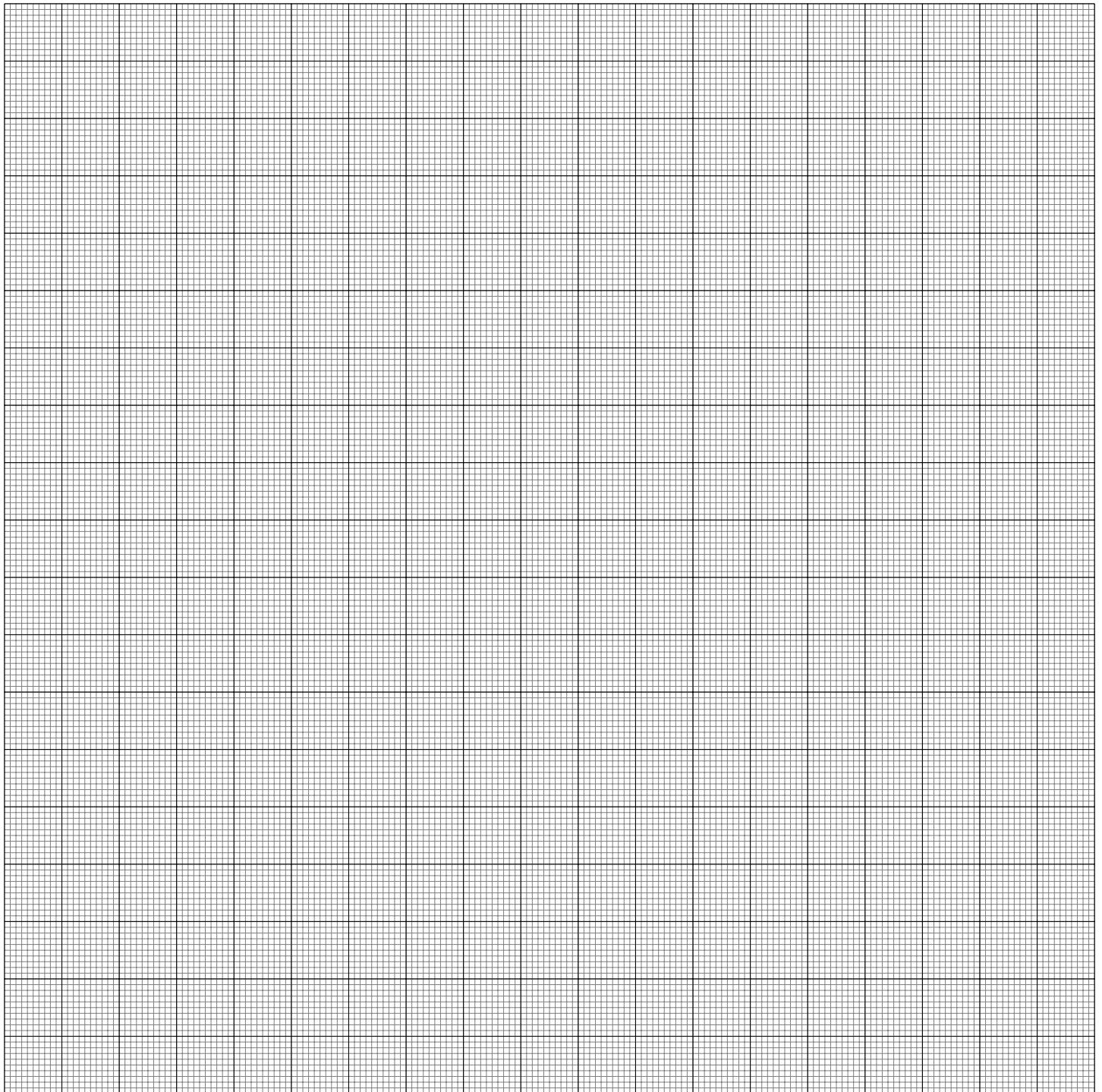Average ΔH (kJ/mol) = ⑦

Average T_m (K) = ⑧

ΔS_{min} (J/molK) = ⑨

Figure 1: time (X axis) vs. Temperature (Y axis)

Post-lab Questions

Entropy and spontaneity

1. Predict the sign of the entropy change for the dissolution of $NaNO_3$

2. Use the data below to compute the entropy change in the dissolution process of sodium nitrate at 298K. Compare your experimental result with the calculated giving reasons for the difference.

	$NaNO_{3(s)}$	$\longrightarrow$	$Na^+_{(aq)}$	+	$NO_3^-{}_{(aq)}$
$S°(J/molK)$	116.32		59.0		146.4
n					
$S° \cdot n$					
$\Delta S°(J/molK)$					

3. Use the data below to compute the enthalpy change in the dissolution process of sodium nitrate at 298K. Compare your experimental result with the calculated giving reasons for the difference.

	$NaNO_{3(s)}$	$\longrightarrow$	$Na^+_{(aq)}$	+	$NO_3^-{}_{(aq)}$
$H°(KJ/mol)$	-466.68		-240.1		-207.36
n					
$H° \cdot n$					
$\Delta H°(KJ/mol)$					

4. Was the dissolution of sodium nitrate spontaneous in the conditions of the experiment?

5. Calculate the value of Gibbs free energy at 298K using the entropy and enthalpy calculated above.