［無機・分析化学標準］

以下の問（１），（２）に答えよ．

（１）無機化合物の反応に関して，以下の問(a)〜(d)に答えよ．

(a) 以下の化学反応式の二つの反応物について，どちらが酸で，どちらが塩基であるか答えよ．また，そのように答えた理由について，Lewis の酸・塩基の定義に基づいて説明せよ．

$$I_2 \quad + \quad I^- \quad \rightarrow \quad I_3^-$$

(b) 以下の配位子交換反応について，反応生成物 **A** の立体構造を描け．

$$[Pt(NH_3)_4]^{2+} \quad + \quad 2HCl \quad \rightarrow \quad \mathbf{A} \quad + \quad 2NH_4^+$$

(c) 金属錯体 ML_nX から ML_nY への配位子交換反応が，解離機構で進行する場合を考える．ここで，M, L, X, Y, *n* はそれぞれ金属イオン，配位子，脱離基，侵入基，L の個数である．M–Y の結合形成が律速段階である場合の反応エネルギー図を，図 1 にならって描け．また，この反応で観測される中間体はどのような化学種か記せ．

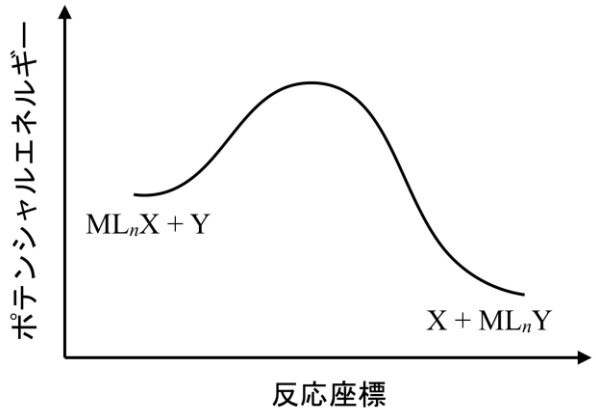

図 1. 反応エネルギー図の例

(d) 化学反応の追跡には様々な分光学的手法が用いられる．以下の[分光分析法]から<u>二つ</u>を選んで，測定原理について簡潔に説明せよ．その際に，[A 群]から適切な語句を一つ，[B 群]から適切な語句を一つ選び，これらの語句を必ず用いて説明せよ．

[分光分析法]
核磁気共鳴法　　マイクロ波分光法　　りん光分析法

[A 群] 測定に用いる電磁波の典型的な波長範囲
1–5 nm　　20–100 nm　　200–800 nm　　1–10 μm　　0.1–100 mm　　0.3–1 m

[B 群] 測定原理に関わる現象
項間交差　光電効果　分子回転　分子振動　Raman 散乱　Zeeman 効果

（2）図 2 に示す塩化ナトリウム NaCl の結晶構造に関して，以下の問(e)〜(h)に答えよ．

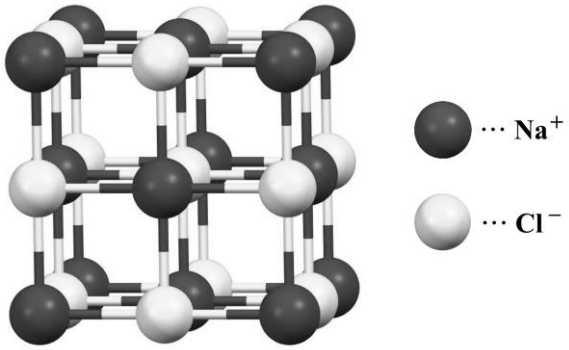

図 2. NaCl の結晶構造

(e) 以下に，NaCl 型結晶構造における Madelung 定数を級数の形で記す．Na^+と Cl^-の最近接原子間距離を 1 とした場合，空欄 $\boxed{x}$, $\boxed{y}$に当てはまる数字を答えよ．なお，級数の第 2 項，第 3 項はそれぞれ中心イオンから 2 番目，3 番目に近いイオンの寄与を表す項である．

$$6 - \frac{\boxed{x}}{\sqrt{2}} + \frac{\boxed{y}}{\sqrt{3}} \cdots$$

(f) NaCl の結晶構造における Schottky 欠陥，Frenkel 欠陥について，それぞれ図を描いて説明せよ．なお，図は平面図でもよい．

(g) 波長 1.54 Å の X 線を用いて NaCl の粉末 X 線回折パターンを測定したところ，$2\theta = 31.6°$に(200)面からの一次の回折が観測された. NaCl の単位格子の長さ *a*, *b*, *c* を有効数字 2 桁で答えよ. また, 必要であれば次の値を用いよ. sin 31.6° = 0.523, sin 15.8° = 0.272, cos 31.6° = 0.852, cos 15.8° = 0.962.

(h) 問(g)の実験後，X 線で照射された NaCl の粉末結晶が変色していた．この変色の原因について簡潔に説明せよ．

[Inorganic and Analytical Chemistry: Standard]

Answer the problems （１） and （２）.

（１） Answer the following problems (a) through (d) concerning inorganic reactions.

(a) In the following reaction, answer which reactant acts as the acid and which reactant acts as the base. In addition, briefly explain the reason for your answer based on the Lewis definition of acids and bases.

$$I_2 + I^- \rightarrow I_3^-$$

(b) Draw the stereostructure of product **A** in the following ligand exchange reaction.

$$[Pt(NH_3)_4]^{2+} + 2HCl \rightarrow \mathbf{A} + 2NH_4^+$$

(c) A ligand exchange reaction from metal complex ML_nX to ML_nY proceeds by the dissociative mechanism, where M, L, X, Y, and *n* are a metal ion, ligand, leaving group, entering group, and number of L, respectively. When the bond formation of M–Y is the rate-determining step, draw the energy diagram of this reaction as shown in the example of Figure 1. In addition, answer the chemical species of the intermediate observed in this reaction.

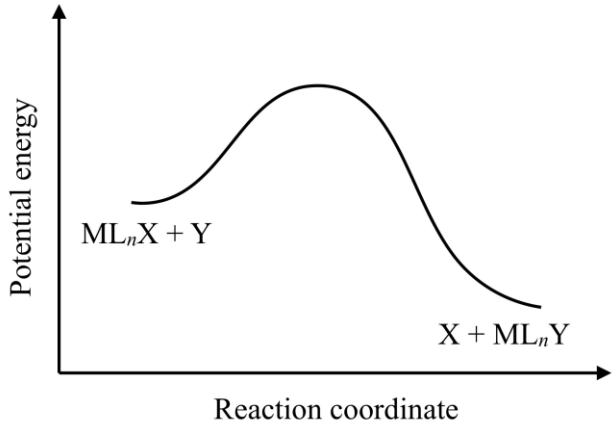

Figure 1. Example of a reaction energy diagram

(d) Several spectroscopic methods are used for the analysis of chemical reactions. Choose <u>two methods</u> from the following [Spectroscopy] and briefly explain their measurement principle, respectively. Note that you must use the most appropriate word of [Group A] and the most appropriate word of [Group B] in the respective explanations.

[Spectroscopy]
Nuclear magnetic resonance spectroscopy
Microwave spectroscopy
Phosphorescence spectroscopy

[Group A] *Typical wavelength ranges of electromagnetic wave in measurement*

1–5 nm, 20–100 nm, 200–800 nm, 1–10 μm, 0.1–100 mm, 0.3–1 m

[Group B] *Phenomena concerning measurement principles*

Intersystem crossing,	Photoelectric effect,	Molecular rotation,
Molecular vibration,	Raman scattering,	Zeeman effect

（2）Answer the following problems (e) through (h) concerning the crystal structure of sodium chloride (NaCl) shown in Figure 2.

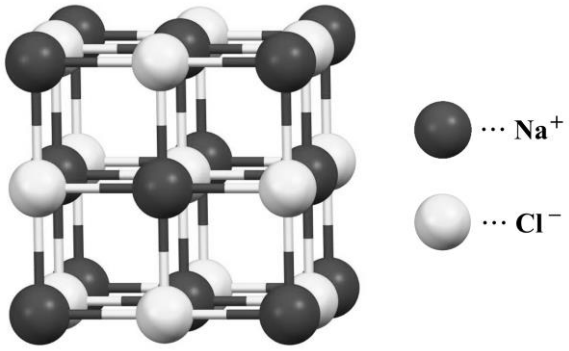

Figure 2. Crystal structure of NaCl

(e) The following series is the Madelung constant of the crystal structure of NaCl. Fill blanks $\boxed{x}$ and $\boxed{y}$. Note that the second and third terms of the series are the terms regarding the second and third nearest neighboring ions from the central ion. The closest atomic distance between Na^+ and Cl^- is assumed to be 1.

$$6 - \frac{\boxed{x}}{\sqrt{2}} + \frac{\boxed{y}}{\sqrt{3}} \cdots$$

(f) Draw figures of the Shottky defect and the Frenkel defect in the crystal structure of NaCl and explain the both defects. You may use two-dimensional figures.

(g) When powder X-ray diffraction pattern of NaCl was measured using an X-ray with a wavelength of 1.54 Å, first-order diffraction from the (200) plane was observed at $2\theta = 31.6°$. Calculate lattice lengths *a*, *b*, and *c* of NaCl with two significant figures. Use the following values, if necessary: sin 31.6° = 0.523, sin 15.8° = 0.272, cos 31.6° = 0.852, cos 15.8° = 0.962.

(h) After the experiment of problem (g), color of the NaCl crystals changed. Briefly explain the cause of this color change.