THERMOGRAVIMETRIC AND DIFFERENTIAL THERMAL ANALYSIS OF MALACHITE AND AZURITE IN INERT ATMOSPHERES AND IN AIR

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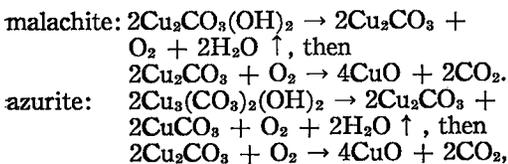*Département de Géologie, Université Laval, Québec, P.Q., Canada G1K 7P4*

ABSTRACT

The rate of dissociation and the degree of stability of malachite, $Cu_2O_3(OH)_2$, and azurite, $Cu_3(CO_3)_2(OH)_2$, in air and in nitrogen, argon and neon were studied over the temperature range 100° to 550°C by TGA and DTA techniques. The solid end-products are CuO and, to a lesser extent, some Cu_2O in the case of the decomposition of azurite in inert atmospheres. The rates of dissociation of malachite and azurite are practically independent of the initial amount of material, and are mainly a function of the temperature, the composition of the gaseous medium in which the reaction takes place, and the grain size. The order of the reaction is approximately one. The activation energies calculated at 83 low to medium temperatures, and extrapolated down to 130°C, vary between 31.4-38.1 and 35.3-46.1 Kcal mole[-1] for the decomposition of malachite in air and inert atmospheres respectively; for azurite, 19.7-43.1 (most commonly around 27.5) in air, and 45.4-59.3 Kcal mole[-1] in inert atmospheres with the formation of up to 12.3% Cu^+ (in Cu_2O) of the total Cu in the solid end-product. In this last case, when CuO only is present as an end-product, the activation energy is of the order of 26.9 Kcal mole[-1].

The stability of malachite and azurite at temperatures lower than 100°-105°C and atmospheric pressure (in air) is definitely due to the presence of the OH radical. The instability or metastability of malachite and azurite in air in the temperature range 105°-215°C is explained by a thin layer of CuO by analogy with the metastability of Al surrounded by a coating of Al_2O_3.
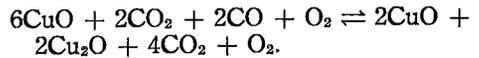
INTRODUCTION

Azurite and malachite are relatively common minerals and are stable at the surface of the earth. Outside their stability fields, malachite and azurite decompose to one or more copper oxides according to the following possible reactions:

malachite: $2Cu_2CO_3(OH)_2 \rightarrow 2Cu_2CO_3 +$
$O_2 + 2H_2O \uparrow$, then
$2Cu_2CO_3 + O_2 \rightarrow 4CuO + 2CO_2$.
azurite: $2Cu_3(CO_3)_2(OH)_2 \rightarrow 2Cu_2CO_3 +$
$2CuCO_3 + O_2 + 2H_2O \uparrow$, then
$2Cu_2CO_3 + O_2 \rightarrow 4CuO + 2CO_2$,
and in the presence of a highly oxygenated atmosphere (air),

$$CuCO_3 \rightarrow CuO + CO_2.$$

However, in the presence of an inert atmosphere

$$2CO_2 \rightleftharpoons 2CO + O_2, \text{ and}$$

$$6CuO + 2CO_2 + 2CO + O_2 \rightleftharpoons 2CuO + 2Cu_2O + 4CO_2 + O_2.$$

The temperature of decomposition of azurite and malachite was investigated by Rose (1851), Kelley & DeNoyer (1960), and Simpson *et al.* (1964). None of these investigators studied the dissociation rates of these two hydrous copper carbonates under isothermal non-equilibrium conditions.

The rate of dissociation (kinetics of mass decomposition), and degree of thermal stability of malachite and azurite in air and in inert gases were examined in the temperature range 320°-445°C to gain some knowledge about the relative importance of grain size, temperature, degree of packing, gaseous medium, and concentration of the reactant (malachite or azurite). These data are used to explain certain characteristics that occur in the general Cu-O-C-S system. The method of study is based on the rate of reaction of any order *n*, whose formula is

$$S = -\frac{dC}{dt} = K_nC^n \dots \dots \dots \dots (1)$$

where S = rate of reaction, C = concentration of the reactant(s) in wt. %, t = time, K_n = rate constant of order *n*, and n = order.

EXPERIMENTAL METHOD

The materials used in all experiments consisted of natural malachite from the Katanga district, Belgian Congo, Africa, and azurite from Bisbee, Arizona, U.S.A. Wet chemical analyses gave 56.7% Cu^{++} in the malachite and 55.7% Cu^{++} in the azurite.

Infrared spectra obtained for both malachite and azurite are similar to the results published by Herzberg (1945), Pfund (1945), Moenke (1960), Huang & Kerr (1960), and Adler & Kerr (1963a, b). X-ray diffraction patterns of the two minerals are similar to those of J. C. P. D. S. patterns of malachite (10-399) and azurite (11-682).

Two types of TGA experiments were performed; one consisted of measuring the variation of mass of the reactants (malachite and azurite) as a function of temperature at a rate of 60°C min⁻¹ (1° sec⁻¹) to produce a thermogram, whereas the other type was a method of isothermal analysis. In the latter case, the temperature was rapidly increased at a rate of 160°C/min up to the temperature chosen and the reactant dissociated at this isotherm during a time interval t.

The thermobalance used was a Perkin-Elmer (Canada) model TGS-1 with a Perkin-Elmer (Canada) temperature controller (model UU-1), a Philips model type PM 8100 dual pen flatbed recorder, and an inert gas circulator. This system has good temperature measurement, a good sensitivity, a rapid cooling rate, and almost instantaneous isothermal equilibrium. The relative accuracy in the measurements of the mass differences is about 0.1% and the temperature control is ±1°C. The experimental procedure is explained in detail by Bouchard (1973). DTA were performed with conventional Fisher Scientific (model 260P and 260F) and Stanton (model Standata −658) DTA instruments against a reference material of Al₂O₃. Ancillary instrumentation included a temperature programmer, and a Fisher Scientific (model PSOIWGA servowriter II) two-pen recorder. Platinum *vs* platinum + 13% rhodium thermocouples were used. The variation in temperature (ΔT) is ± 2°C. The programmed temperature rate was 10°C min⁻¹ and sample mass varied between 150-300 mg. A detailed description of the experimental DTA procedure is given in Moreau (1971).

The experiments were conducted in free air and in an inert gas at the ambient temperature. Intentionally, neither CO nor CO₂ was circulated through the system.

All crystalline products were identified by x-ray films obtained with 114.6 mm Debye-Scherrer and Guinier focusing cameras. Supplementary infra-red scanning was also performed on some of the solid end-products. Because disorder in the structures of many of the end-product(s) made it difficult to determine whether the copper oxide was tenorite (CuO), cuprite (Cu₂O) or paramelaconite (6CuO.Cu₂O), about eighty of the end-products were chemically analyzed for Cu⁺⁺ and Cu⁺ by titration of Cu⁺ with dichromate. Occasionally a reflected light microscope with high-power oil immersion objective lenses was used to observe the spatial progression of the dissociation and oxidation of malachite and azurite grains.

PROCEDURE

For the TGA experiments, the calculations are made with the ratio of the material associated at time t over the total amount dissociated at infinite time ($t = \infty$). In practice, the time for complete dissociation can be considered as finite (*e.g.* time at 99.3 or 99.8 per cent dissociation). Then the percentage of malachite or azurite dissociated was plotted against log time. Integrating equation (1), the order n is obtained through the following formula:

$$K_n t = \frac{1}{n-1}\left[\frac{1}{C^{n-1}} - \frac{1}{C_o^{n-1}}\right] \text{for } n \neq 1$$

or

$$K_n t = \frac{1}{(n-1)C_o^{n-1}}\left[\left(\frac{C_o}{C}\right)^{n-1} - 1\right] \quad (2)$$
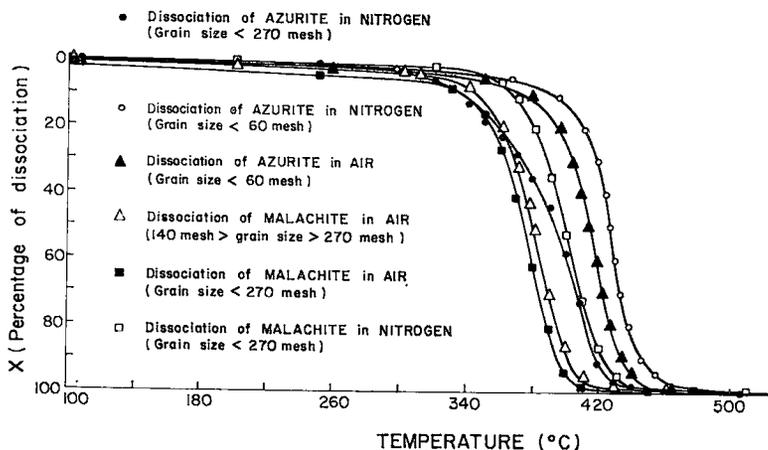

FIG. 1. Dissociation of malachite and azurite as a function of temperature in nitrogen and air.

The concentration of the reactant is expressed in percentage and the order of the reaction is determined with the help of the decomposition temperatures.

EXPERIMENTAL RESULTS

Some 83 experiments were conducted with the thermobalance. Eleven experiments were duplicated to demonstrate the reproducibility of the results obtained. Figure 1 shows the results of the dissociation of malachite and azurite as a function of temperature in nitrogen and in air. Table 1 gives the experimental details for each data set, from which curves as illustrated in

TABLE 1. RESULTS OF THE EXPERIMENTS

Run No.	E (Kcal mole^{-1})	Material	Grain Size (Mesh)	Gas	Temperatures of iso-therms (°C)
1	31.6	malachite	<270	air	425,405,395,380,365,350
2	37.5	malachite	140-270	air	415,395,380,365,350
3	38.1	malachite	>140	air	425,405,395,380,365,350
4	45.8	malachite	<270	N$_2$	400,380,360,350,340
5	36.8	malachite	140-270	N$_2$	400,370,350,340
6	35.4	malachite	>140	N$_2$	400,380,370,360,350,340
7	43.1	azurite	<270	air	415,405,385,373,355
8	27.5	azurite	140-270	air	415,400,380,370,350
9	18.7	azurite	<60	air	410,395,385,375,360
10	49.3	azurite	<270	N$_2$	415,400,385,375,360
11	45.4	azurite	140-270	N$_2$	405,395,385,375,360
12	26.9	azurite	<60	N$_2$	410,390,380,365

Figures 2 and 3 were obtained. By calculating the mean of the rate constants K for each of the experimental isothermal experiments, they can then be compared with the theoretical iso-

ISOTHERMAL DISSOCIATION OF MALACHITE IN AIR
(Grain size < 270 mesh)

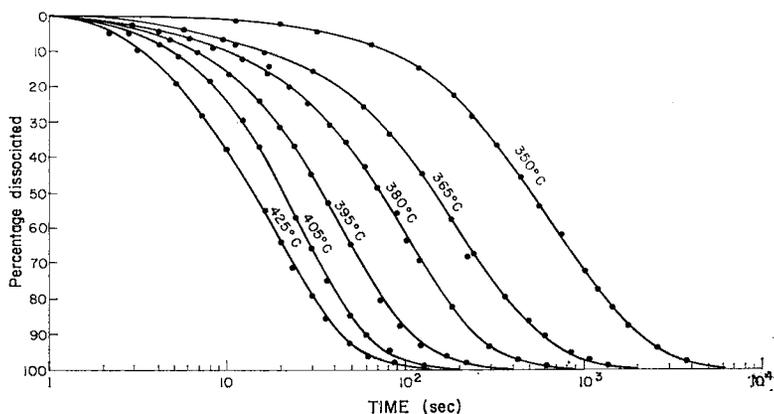FIG. 2. Isothermal dissociations of malachite in air (grain size <270 mesh).

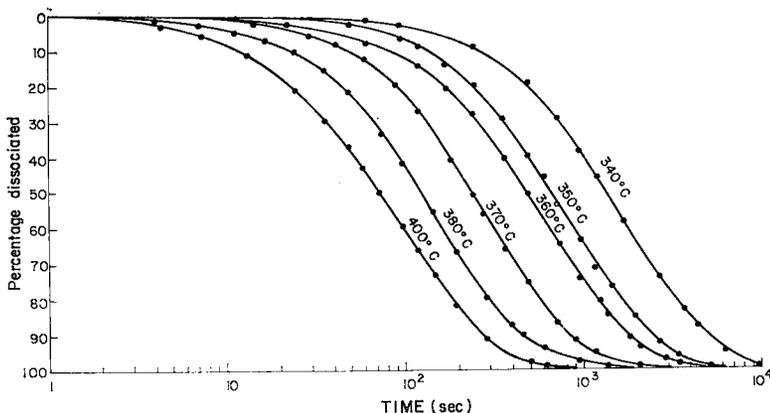ISOTHERMAL DISSOCIATION OF MALACHITE IN NITROGEN
(Grain size > 140 mesh)

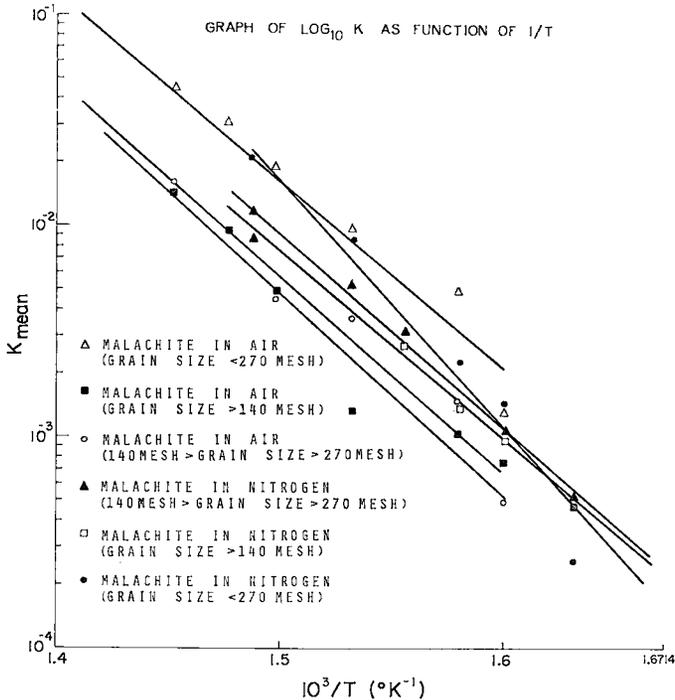FIG. 3. Isothermal dissociations of malachite in nitrogen (grain size >140 mesh).

FIG. 4. Activation energy for the dissociation of malachite in air and in nitrogen in the temperature range 310°-450°C for different grain sizes.

thermal curves. It was then established for the malachite and azurite reactions that the rate of dissociation is independent of the initial amount of reactant, and that the reaction order calculated from individual sets of experiments ranged from 1.0 to 1.1, and consequently the first order was adopted.

The experimental results illustrated in Figure 1 indicate that, for a grain size less than 270 mesh (Tyler sieve), the dissociation of malachite in air is faster than for a grain size larger than 270 mesh. The dissociation of malachite in air is similar for grain sizes ranging between 140 and 270 mesh. Similarly, in a nitrogen atmosphere, the finer-grained malachite dissociates faster. Finally, for an arbitrary grain size and a fixed temperature, malachite dissociates faster in a nitrogen or argon atmosphere than in air.

Azurite of –270 mesh dissociates faster in air than coarser material, and azurite between 140-270 mesh dissociates faster in air than 60 mesh material. In a nitrogen or argon atmosphere, the finer the grain size of azurite, the faster the dissociation. Finally, for an arbitrary grain size and a given temperature, the azurite dissociates faster in a nitrogen atmosphere than in air for larger grain sizes, but faster in air than in a nitrogen atmosphere for fine grain sizes.

INTERPRETATION OF RESULTS

Once the rate constant K_1 is found, the activation energy of the reaction can be calculated with Arrhenius' formula. A plot of log K_1 against $10^3/T$ gives a straight line with a slope of $E/4.576$. As the order, rate constants, and temperatures are known, the activation energy is calculated from low- to medium-temperature runs (310° to 450°C) of the dissociation of malachite, and extrapolated down to 130°C (approximate metastability limit of malachite in air). In the approximate range 130° to 450°C and for different grain sizes, the calculated activation energy related to the dissociation of malachite varies between 31.6 and 45.8 Kcal mole^{-1} (Table 1). Except for the two extreme values of E when the grain size is very small, the activation energy accompanying the dissociation of malachite varies between 35.4 and 38.1 Kcal mole^{-1}, which is a relatively narrow range. Figure 4 shows a diagram of log K_1 vs $10^3/T$ for the experiments performed in air and in a nitrogen atmosphere. The activation energies are calculated directly from these experimental results. The activation energy for the dissociation of azurite was calculated in the same fashion. The activation energy related to the dissociation of most natural azurite is about 25 to 27 Kcal

mole^{-1}. Roth (1941) calculated the heats of formation for malachite (13.8 Kcal mole^{-1}) and azurite (20.9 Kcal mole^{-1}).

The dissociation of malachite is a direct reaction involving no intermediate products. CuO is encountered as an end-product at all temperatures investigated; the other possible end-product is less than 1.7% Cu$_2$O. Similarly, CuO is the only solid end-product formed from the dissociation of azurite in air. However, in a nitrogen atmosphere, the dissociation is more complex and involves the formation of some Cu$_2$O. The ratio of Cu$_2$O:CuO is function of CO:CO$_2$, that is, the fugacity of O$_2$. The formation of Cu$_2$O decreases the CO$_2$ concentration, because Cu$_2$O eases the outward diffusion of the large polar molecules of CO$_2$ which would otherwise be slowed by the surface layers of CuO during the oxidation process. The lag related to oxidation of Cu$_2$O does not take place, and this accelerates the dissociation process.

The presence of a CuO coating slows the diffusion of CO$_2$ more in larger grains as their external contacts are minimal. CO$_2$ attempting to escape through the first coating of oxide partly dissociates to CO and O$_2$, thus favouring the formation of a thin coating of Cu$_2$O and the escape of CO$_2$, CO and O$_2$ from the internal reaction shell of the oxide coating. In this fashion, the reaction speeds up for coarser grain sizes.

DTA curves were obtained for malachite and azurite at 1 atmosphere pressure. The dissociation of malachite began at 310°C and ended at 420°C, with a peak at 375°C, whereas it occurs in the temperature range 290° to 395°C for azurite with a peak at 350°C. According to Beck (1950a, b) malachite decomposes at 45°C less than that of azurite, but such a difference has not been noted by Heystek & Schmidt (1954), Kleber & Gürtzsch (1966) or in the present study. For both hydrous copper carbonates, the endothermic peak represents the release of the water molecules (100°C), but it is more evident in the case of azurite (Fig. 5).

According to the theory of Borchardt & Daniels (1957), the variations in enthalpy (ΔH_R) or heat of reaction (decomposition) can be calculated from the DTA curves. The quantity of heat absorbed or released during a reaction is proportional to the area under the DTA curves. The instrument was calibrated with a standard FeO(OH) sample, trade mark Mapico, manufactured by Columbian Carbon Canada Co., Ltd., Montreal 16, P.Q., and Mapico, Cities Service Co., U.S.A. Its DTA curve shows an endotherm that peaks at 330°C and extends from 230° to 360°C. The variation in enthalpy (ΔH_R) of this
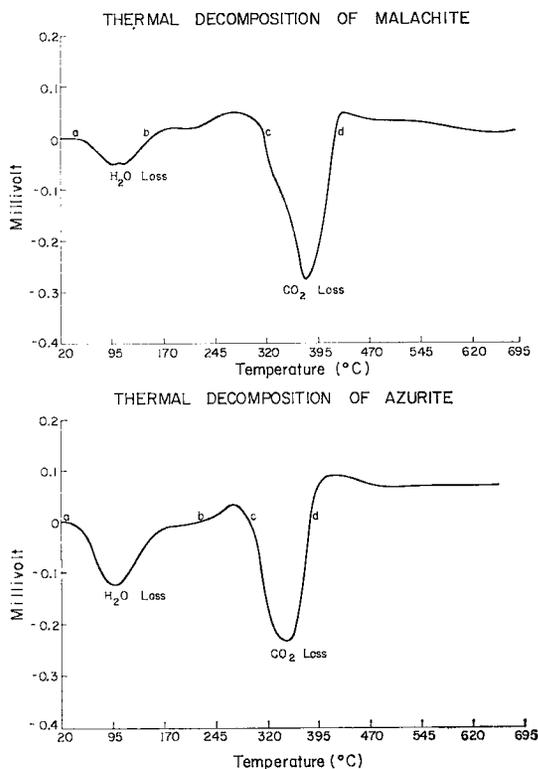

FIG. 5. DTA curves of the decomposition of malachite and azurite in air (1 atmosphere pressure) for a programmed heating rate of 10°C min^{-1}.

dehydration of FeO(OH) is 16.0 Kcal mole^{-1} of H$_2$O and the equivalent area under the curve is 4.443 V°C per molecule weight. The equivalent area under the curve for the decomposition of azurite is 10.35 V°C per molecular weight of CO$_2$ dissociated, and consequently the variation in enthalpy is about 37.2 Kcal mole^{-1} (grain size less than 270 mesh) in air. The equivalent area under the curve for the decomposition of malachite is 11.81 V°C per molecule of CO$_2$ dissociated, and the the variation in enthalpy is about 42.3 Kcal mole^{-1} (grain size less than 270 mesh) in air.

CONCLUSION

In the temperature range 300° to 500°C, the rate of dissociation of malachite and azurite is independent of the initial amount of material. Consistently similar results were obtained for experiments with malachite or azurite concentrations diluted by inert components with various degrees of packing. In order of importance, the rate of dissociation is a function of the temper-

ature, the grain size, and the gaseous medium in which the reaction takes place. The heating rate is another important variable when decomposition does not take place at a fixed temperature. A first-order reaction is established for the dissociations. At low temperatures ($105°$-$200°C$), the rate of oxidation is faster than the rate of dissociation.

For all practical purposes malachite and azurite persist indefinitely at temperatures lower than $95°C$. Between $95°$ and $210°C$, malachite and azurite are metastable to unstable in air and nitrogen, depending mainly on the grain size and, to a lesser extent, on the heating rate. In the case of malachite, a smaller grain size and total binding energy is associated with a larger surface energy per unit volume, which favours outward diffusion of the large polar CO_2 molecules and extensive oxidation to CuO by the surrounding medium (air). Therefore, the activation energy is greater for larger grain sizes when the decomposition of malachite takes place in air, and is less for larger grain sizes when the decomposition takes place in nitrogen. For azurite the activation energy is smaller for larger grain sizes, whether the decomposition occurs in air or an inert atmosphere. At higher temperatures of decomposition, and in an inert atmosphere in particular, the CO_2 molecules diffuse relatively slowly and the oxidation of the grain exterior to CuO takes place progressively. In the case of smaller grain sizes, the CO_2 molecules diffuse more rapidly and an equilibrium of $2CO_2 \rightarrow 2CO + O_2$ is readily established with the ambient gaseous medium. A secondary reaction ($2CuO + CO_2 \rightleftharpoons Cu_2O + CO_2$) then takes place for a fraction of the CuO, which explains the presence of Cu_2O mixed-layers around an azurite grain in the decomposition process. At temperatures higher than $225°C$, malachite and azurite are definitely unstable and dissociate readily.

ACKNOWLEDGEMENTS

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