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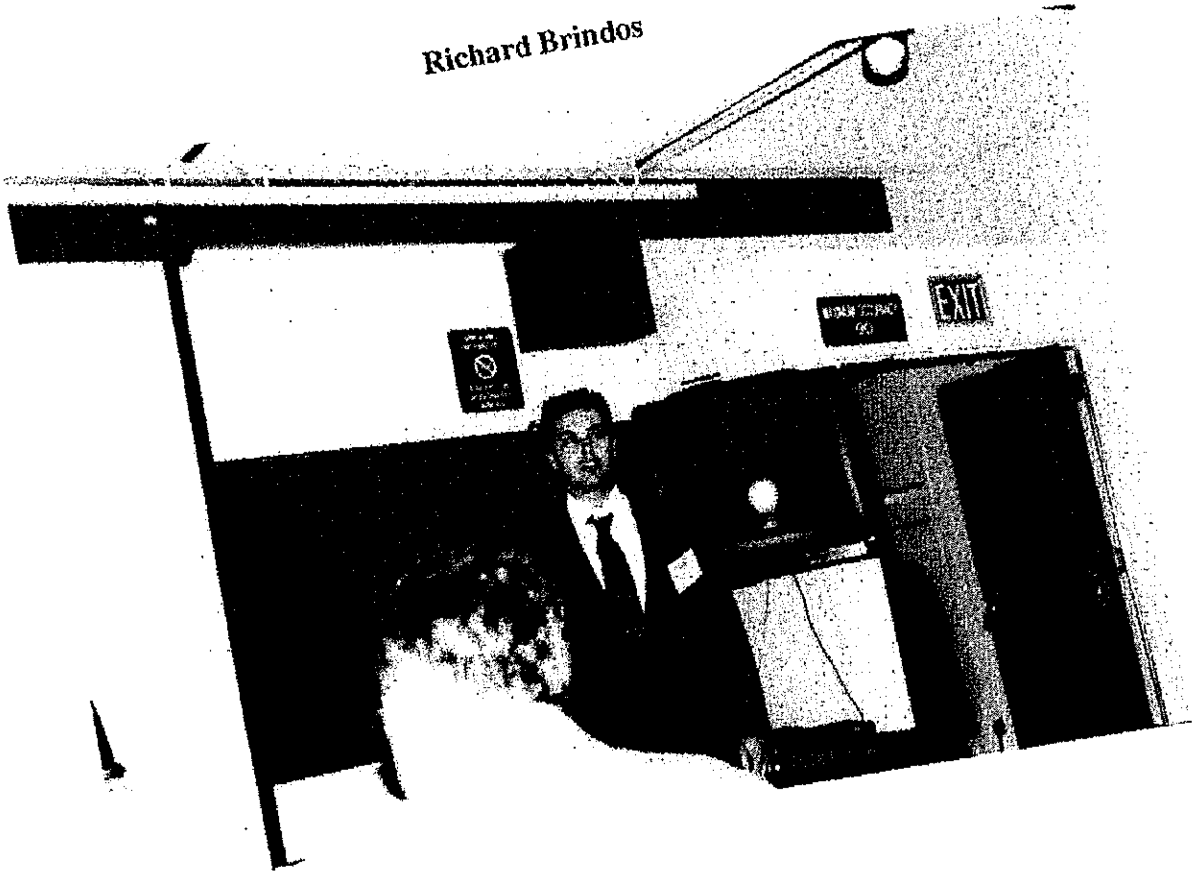

Effect of Temperature on Wetting Angle

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Key Words

Wetting, Sessile Drop, Contact Angle, Wetting Angle

Prerequisite Knowledge

Background in the phenomenon of wetting would be helpful in the understanding of this lab experiment.

Objective

To determine the effect of temperature on the contact (or wetting) angle of a liquid-solid system, an example being molten solder on a copper substrate.

Equipment and Supplies

1. Contact Angle Measurement System
2. 99.99% Copper strips: 4.1 ±0.1 cm x 1.3 ±0.1 cm x 0.06 ±0.01 cm
3. Solder
4. Liquid Solder Flux
5. Argon gas
6. Acetone
7. Methanol
8. Ultra-sonicator
9. Plastic Tweezers
10. Protractor
11. Bright pen
12. 15 cm ruler

A contact angle measurement system was designed and constructed for this experiment.

Drawings of this system are available from G. Selvaduray upon request.

Introduction

The phenomenon of wetting is very important in many cases, both industrially and otherwise. One example of an industrial application where wetting plays a critical role is in the formation of brazed and soldered joints. The application of wax on automobile paint reduces the tendency of the paint to be wet by water. Similarly, in the kitchen non-stick frying pans have that name because they are not wet by water or oil. The topic is also of critical importance in the application of adhesives. Wetting can be explained using the following example. Immerse a solid in a liquid (e.g. a glass slide in water) and then remove it. If the liquid adheres to the solid as the piece is removed then the liquid is said to have wet the solid. On the other hand, if the liquid beads up into spherical balls and does not stick to the solid, then the liquid does not wet the solid. Another very common example of non-wetting is liquid mercury placed on glass; the liquid mercury will form small spheres and not stick to the surface.

The wetting behavior of a liquid on a solid can be characterized by the wetting or contact angle that is formed between the liquid and the solid substrate. Contact angle studies are commonly done by using the Sessile Drop Method. A "sessile drop" is a continuous drop of liquid on a flat, solid surface under steady-state conditions. To neglect the effects of gravity, the gravitational forces should be small compared to the surface tension of the drop.[1] If this condition is satisfied, the drop will approach a hemispherical shape which represents its smallest area and lowest surface free energy. The sessile drop is placed on the solid substrate and the angle between the solid surface and the tangent to the liquid surface at the contact point is measured. This is known as the contact angle or wetting angle. The contact angle can vary between 0 and 180° and is a measure of the extent of wetting. The conditions of good wetting (θ<90°) and partial-wetting (θ>90°) are illustrated in Figure 1. Complete wetting (also referred to as spreading) is obtained at an angle of 0° and complete non-wetting occurs at an angle of 180°.

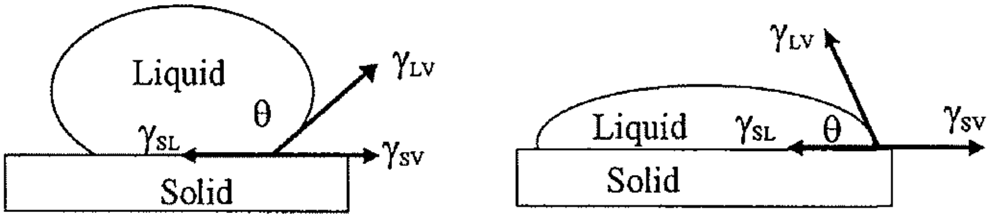

Figure 1: The sessile drop to the left is an example of poor wetting (θ>90°), and the sessile drop to the right is an example of good wetting (θ<90°).

The contact angle is the vector sum of the interfacial surface energies between the solid/liquid (γ_{SL}), liquid/vapor (γ_{LV}), and solid/vapor (γ_{SV}) phases. The change in surface free energy, ∂F, with a small change in solid surface covered, ∂A, can be determined by the Young and Dupre equation.[1]

$$\left(\frac{\partial F}{\partial A}\right)_{P,T} = \gamma_{LV} + \gamma_{SL} - \gamma_{SV} \tag{1}$$

where, γ_{SV} = Solid/Vapor surface energy
γ_{SL} = Solid/Liquid surface energy
γ_{LV} = Liquid/Vapor surface energy.

The surface free energy change can also be approximated in terms of the change in surface area and contact angle, θ, as follows:

$$\Delta F = \Delta A(\gamma_{SL} - \gamma_{SV}) + \Delta A \gamma_{LV} \cos(\theta - \Delta\theta) \tag{2}$$

As the system approaches equilibrium,

$$\lim_{\Delta A \to 0} \frac{\Delta F}{\Delta A} = 0 \tag{3}$$

and

$$\gamma_{SL} - \gamma_{SV} + \gamma_{LV} \cos\theta = 0 \tag{4}$$

Equation 4 can be rewritten in the form of the well known Young's equation as

$$\gamma_{LV} \cos\theta = \gamma_{SV} - \gamma_{SL} \tag{5}$$

The driving force for wetting is (γ_{SV} - γ_{SL}). The balancing force is the horizontal component of the surface tension of the liquid ($\gamma_{LV}\cos\theta$).

Young's equation represents a steady-state condition for a solid/liquid interface in stable or metastable thermodynamic equilibrium. However, there is no definite indication of whether chemical or van der Waals bonding exists, other than that the contact angle is generally smaller with chemical bonding, as compared to that in the presence of van der Waals bonding.[1] The contact angle, or extent of wetting, is dependent on the interface between the liquid and the solid. The nature of the surface of the solid, especially its cleanliness, will affect the interface and therefore also the contact angle.

Temperature changes have also been shown to affect the contact angle of many different systems.[1-6] The temperature effect, in most cases, can be explained by a reaction at the liquid/solid interface. Thermally activated reactions can occur due to the fact that many systems are not at chemical equilibrium. The reactions that contribute to wetting (decrease of the contact angle) are those that increase the driving force for wetting (γ_{SV} - γ_{SL}), which is acting at the surface of the liquid drop and the solid substrate. The reactions that contribute to the driving force for wetting are the ones in which the composition of the substrate changes by dissolution of a component of the liquid. On the contrary, if the reaction results in a change of the liquid's composition by dissolution of the solid substrate, but with no change in the composition of the substrate, there is no contribution to the driving force for wetting.[2]

As mentioned above, if the solid substrate is an active participant in the reaction, the free energy of the outer surface of the liquid drop will contribute to the driving force for wetting. As the drop expands on the substrate, the perimeter remains in contact with unreacted solid and thus the reaction continues to contribute to the driving force for wetting. Examination of phase diagrams representing the interaction between the constituents of the liquid and solid surfaces can help to predict the wetting behavior of a system.

Young's equation (Equation 5) for a non-reacting, steady-state drop can be modified to include the contribution of the free energy of reaction[2]

$$\gamma_{SV} - \left(\gamma_{SL} + \frac{\Delta G_R}{dA,dt}\right) \geq \gamma_{LV}\cos\theta \tag{6}$$

The free energy required for the increase of the surface area of the drop as the perimeter expands provides the only resisting force to the expansion. It can be shown thermodynamically that the driving force for wetting does not exceed γ_{LV}, resulting in a steady-state contact angle.[8] A dynamic contribution exists until the liquid is consumed in the reaction, equilibrium compositions are attained, or the temperature is lowered to terminate the reaction.

During a non-spreading reaction, one in which the composition of the substrate does not change, the contact angle may also change. In the early stages of an experiment, spreading due to reaction should be distinguished from the slow rate of movement toward the equilibrium contact angle that a highly viscous nonreactive liquid undergoes in reaching its thermodynamic equilibrium.

The Sessile Drop Method

One of the most common methods for measuring the contact angle is the sessile[*] drop method, which involves depositing a liquid drop on a solid surface and measuring the angle between the solid surface and the tangent to the drop profile at the drop edge. The material intended to be molten can either be placed on the substrate as a solid and heated to its melting temperature or it can be heated in a syringe type device and a single drop can be placed on the solid substrate. The contact angle is then measured with the aid of a contact angle goniometer. The contact angle can be measured directly with a protractor or by using an equation relating the height and radius of the drop to the angle obtained. The sessile drop method is the most widely accepted method for determining the contact angle due to the simplicity of obtaining reliable data.

A system capable of measuring the contact angle as a function of temperature has been designed and constructed by the authors, as an integral part of Richard Brindos' senior project. A detailed explanation of the system is contained in Brindos' senior project report.[9] The Contact Angle Measuring System (CAMS) is illustrated in Figure 2.

The three main components of the CAMS are the tube furnace, experimental tube and monitoring system. The general construction of the system is as follows: the experimental tube fits, anchored, inside the tube furnace and the specimen is loaded into

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[*] The word "sessile" comes from the Latin *sessilis* which means "to sit". Thus, the sessile drop method utilizes a drop that "sits" on a substrate.

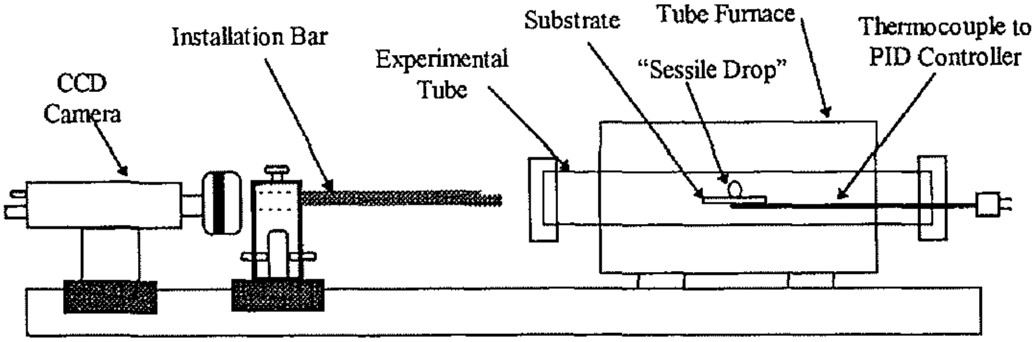

Figure 2: Conceptual design for the Contact Angle Measurement System.

the center. The experimental tube is sealed by caps that allow for specimen visualization on the monitoring side and thermocouple insertion through the opposite side. The caps are also designed to support fittings for the gas inlet and outlet, which provide atmosphere control. A CCD (Charged Coupled Device) camera focuses at the center of the tube and midway down the furnace. The specimen image is displayed on a 13 inch, black and white video monitor . The specimen can be examined continuously during an experiment through the window in the monitoring cap. The CCD camera is also coupled to an IBM personal computer, which is capable of capturing still photos of the image upon operator request. The images can be saved for later image analysis and printout. The assembled system is shown in Figure 3.

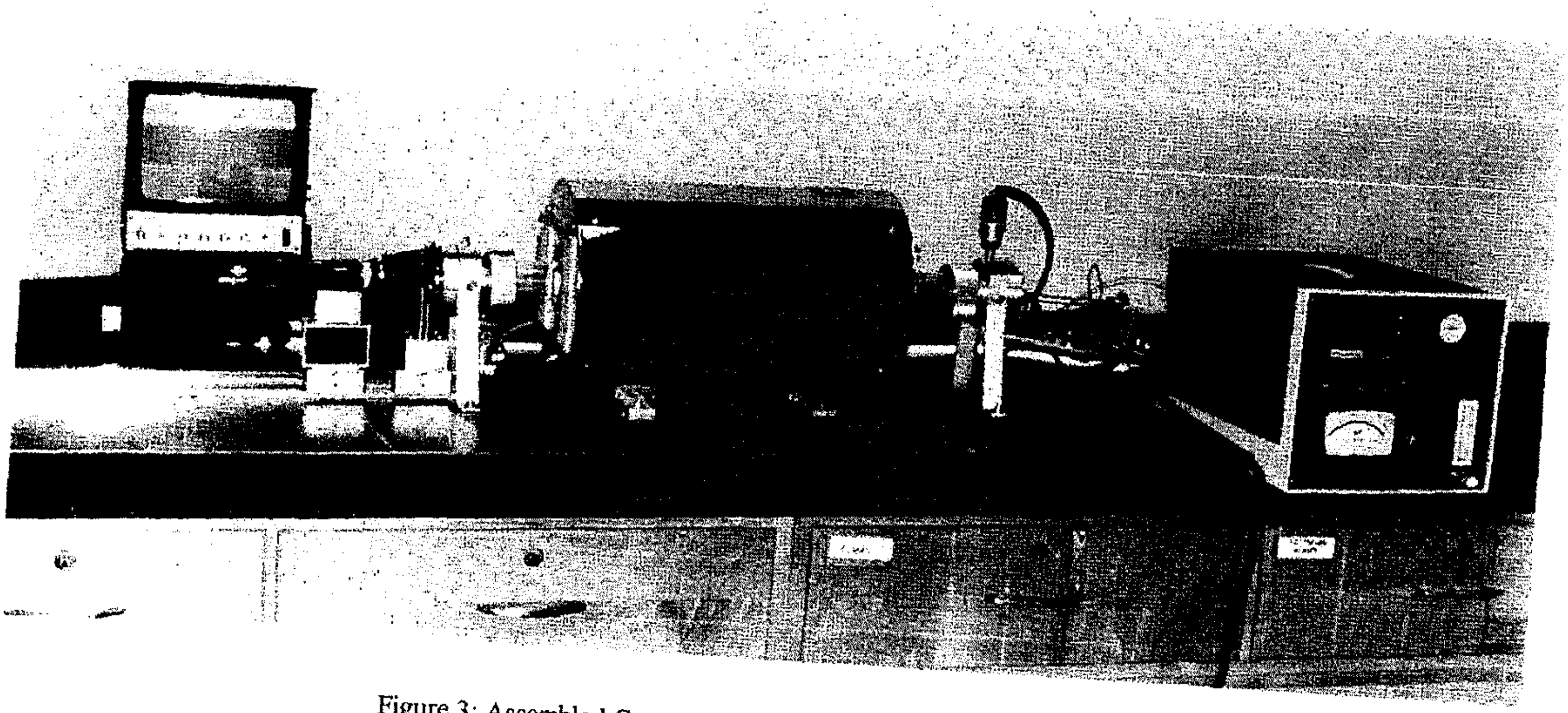

Figure 3: Assembled Contact Angle Measurement System (CAMS).

Experimental Procedure

1. Determine the heating schedule needed and program the furnace controller according to the controller instruction manual. (An example of a heating schedule is shown in Appendix B).
2. Slice copper strips into 4.1 ±0.1 cm x 1.3 ±0.1 cm x 0.06 cm ±0.01 .
3. Cut pieces of solder ≈ 0.25 cm dia x 0.25 cm thick.
4. Ultrasonically clean the copper and solder in methanol to remove any surface contamination.
5. Rinse in acetone and allow to air dry.
6. Using plastic tweezers, dip copper strip into the flux and then place it on the installation bar as noted in the CAMS directions.
7. Using plastic tweezers, dip the solder ball into the flux and then place it centered on the copper strip as illustrated in Figure 4.
8. Load the specimen into the center of the CAMS experimental tube.
9. Seal the window end cap and begin atmosphere control procedures as outlined in the manual.
10. Flush the system adequately by flowing argon through it.
11. Start the heating sequence.
12. When the solder reaches the melting temperature begin to snap pictures at set temperature intervals (approximately 1 picture per 10°C rise in temperature) through 350°C.
13. Print out each image obtained.
14. With a bright pen draw a line tangent to the melt surface and one even with the substrate. An example is shown in Figure 5.
15. Measure the angle between these lines and record the temperature and measured contact angle in Table 1.
16. Plot the measured contact angle versus temperature. An example is shown in Figure 6.

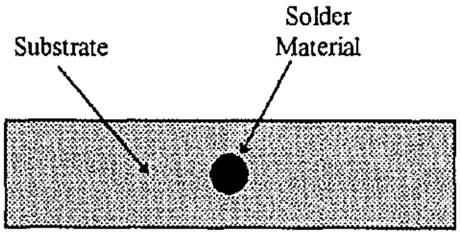

Figure 4: Illustration of solder placement on the substrate.

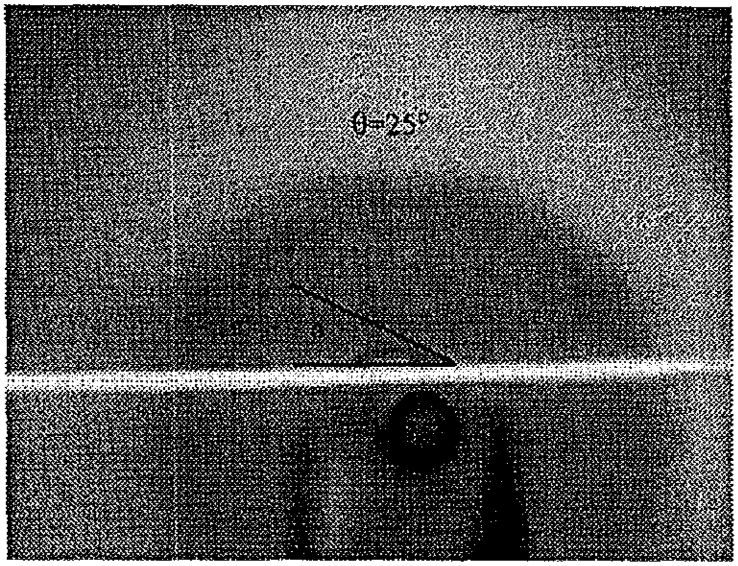

Figure 5: Example of contact angle measurement.

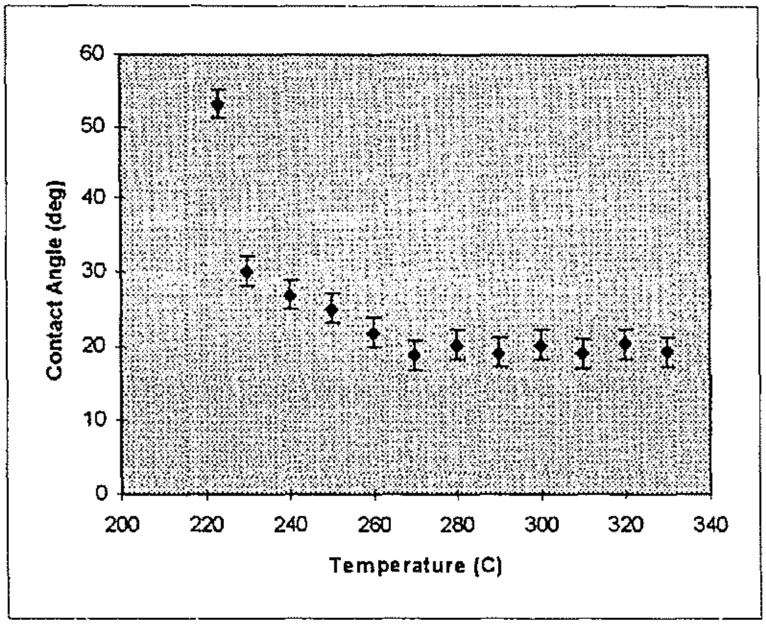

Figure 6: Example of the plotting of the data.

Table 1: Measured contact angles at various temperatures.

Liquid Composition:	Substrate Material:
Temperature (°C)	Contact Angle (deg.)
223	
230	
240	
250	
260	
270	
280	
290	
300	
310	
320	
330	

Discussion Questions:

1) What are the factors that could change the wetting angle?
2) Would the wetting angle change if the same solder was placed on a different substrate?
3) What role does temperature have in the wetting process?
4) Is there a way to predict the interaction between the liquid and solid?
5) Does the Pb-Sn solder alloy with the copper substrate? How do you know that it does or does not?

Richard Brindos' senior project report, which contains details of construction and operation of the CAMS, can be obtained by contacting G. Selvaduray at San Jose State University.

Acknowledgments

The authors wish to thank Raymond Brindos, Central Services, College of Engineering, for his significant contributions in the design and construction of the CAMS system. Without Ray's invaluable help this project would not have been possible.

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BRIEF BIOGRAPHIES

Richard Brindos graduated with a B.S. degree in Materials Engineering from San Jose State University. He is currently pursuing his Ph.D. in Materials Science and Engineering at the University of Florida, Gainesville, Florida.

Guna Selvaduray is Professor, Materials Engineering Department, San Jose State University. He is the Director of the Engineering Ceramics Laboratory and Area Coordinator for the M.S. program in microelectronic packaging. Guna has broad and interdisciplinary research interests that span microelectronics, materials processing, corrosion, ceramics and recyclability of engineering materials.