*GASOLINE ADDITIVE*

INTRODUCTION

**Description**

Students determine the freezing point depression constant, $K_f$, of t-butanol. They then calculate the amount of ethanol that should be added to 1 kg of t-butanol to keep it fluid at -10°F.

**Goals for This Experiment**

The goals for this experiment are to have students:

1. determine the freezing point depression constant of t-butanol by graphing, and
2. answer the question posed by the scenario.

**Recommended Placement in the Curriculum**

Students do not need prior knowledge of colligative properties. However, to fully understand the process occurring in the lab, freezing point depression should be covered before they answer all the questions.

## GASOLINE ADDITIVE

### BACKGROUND
Unleaded gasoline currently contains compounds known as oxygenates which are responsible for increasing the octane rating and reducing engine "knocking." Oxygenates also reduce carbon monoxide emissions. MTBE and ETBE (Methyl-t-Butyl Ether and Ethyl-t-Butyl Ether) are examples of oxygenates along with methanol and ethanol. Ethanol (the alcohol component of gasohol) will increase the octane value approximately one unit for about each 3% ethanol added. Research with pure alcohol fuels shows better performance with ethanol. In addition, the current political climate with respect to farm-grown fuels favors ethanol (and by extension ETBE) as gasoline additives.

### SCENARIO
Consider that a Midwestern producer of ethanol for fuel has just been approached by an entrepreneur who is considering producing a specialty gasoline additive product. The approximate composition of this product is 80% ethanol, 12% t-butanol (also an oxygenate and additionally a gasoline de-icer) and 8% combined smaller additive components. The ethanol will be available locally, but the t-butanol will need to be shipped in from a petrochemical producer. The t-butanol is usually handled as a liquid; it is shipped and stored in bottles, solvent drums, and tank cars. However, it has a freezing point of 25°C (77°F). All containers of the material will need to be heated and melted during the fall, winter, and early spring months before mixing, which will be expensive. An engineer has suggested that some ethanol be added by the manufacturer to the t-butanol before it is shipped to keep it from freezing. You have been asked to determine how much ethanol should be added to keep the ethanol–t-butanol mixture fluid at -10°F. In order to determine your level of profitability, you must determine how much of the locally produced ethanol the specialty gasoline additive will contain.

### SPECIAL DIRECTIONS
To work this scenario, the freezing point depression constant of t-butanol must be determined. This constant can then be used to estimate how much ethanol must be added to t-butanol for winter shipment to the Midwestern plant. An argument could be made for simply looking up the freezing point depression constant, but freezing points are very dependent on purity of materials so it is advisable to use the actual material which will be used in the gasoline additive product shipments. The cooling curve of pure t-butanol will be obtained first, followed by the cooling curve with successive amounts of ethanol added. The rate of cooling will be kept constant by using a cold water bath during the temperature measuring process.

### PROCEDURE
A thermometer calibrated to 0.2 or 0.1°C will give the best results. Be sure to give the thermometer at least 10 seconds between readings to register a new temperature. Experience has shown that the data will be better with the digital thermometer than the large-bore, red alcohol thermometers usually used in the introductory laboratory.

**Q 1:** A temperature change of 0.1°C corresponds to what size temperature change in °F?

**I. Determination of the Freezing Point of t-butanol**

1. Weigh a large, clean, dry test tube and 100 mL beaker. (The beaker is used to support the test tube in an upright position.)

2. Add 30 mL t-butanol to the test tube. Reweigh the test tube and beaker.
   ⇒ Calculate the mass of t-butanol used.

3. Locate a two- or three-hole stopper assembly that will accommodate the thermometer and a wire stirrer. Put the stirrer in place and fit the stopper and thermometer in place on the test tube.
   *Be sure that the stirrer hole has extra space to open the system to the atmosphere; it is dangerous to heat a closed system. See model set-up if necessary and/or available.*

4. Warm the test tube and contents in a warm water bath until the temperature of the t-butanol is about 50°C.
   *Hot tap water is sufficient for the water bath. Depending on the size of the test tube, the bath size may be important. A bath of a 600-mL beaker is suggested for both heating and cooling.*

5. Fill a 600-mL beaker with cold water and add ice until the temperature of the mixture is between 10 and 5°C. (The red alcohol thermometer is OK for this temperature check.) Excess ice may be removed, but you may want to leave a couple ice pieces in the bath to keep the temperature constant while the bath is used and the bath warms slightly.

6. When the temperature of the t-butanol in the test tube while in the warm water bath registers about 50°C, the test tube is ready to be lifted out of the warm water bath and immersed in the cold water bath.

   ***Note: The next task will be easier if one member of the pair stirs and reads the thermometer, while the other person watches the clock, tells when to read the temperature, and records the values found.***

7. Immediately after placing the test tube in the cold water bath, stir the test tube contents with the wire stirrer and begin recording the temperature of the t-butanol in the test tube every 15 or 20 seconds. Continue recording the time and temperature of the t-butanol until the material in the test tube is solid (or until the stirrer is frozen in the alcohol.) After you can no longer stir the alcohol, continue taking temperature readings for another minute.

8. The test tube assembly may then be warmed in the hot water bath until the t-butanol is melted and warmed. Repeat the procedure to obtain another set of data for a cooling curve.
   ⇒ A plot of temperature versus time should give reproducible changes in slope at the freezing point. If the graphs are not reproducible, a third determination may be necessary.

***Note: Since you have two sets of data, one member of the pair should graph one set while the other person graphs the second set. Then share your results.***

**II. Determination of the Freezing Point Depression Constant of t-butanol**

1. Reweigh the test tube containing the t-butanol (the 100-mL beaker is necessary here also).

2. The ethanol should be in small dropper bottles. Add about 0.75 grams of ethanol to the t-butanol to the test tube. (15 to 20 drops is close to 0.75 grams.) After adding the ethanol to the test tube, reweigh the assembly.
   ⇒ Determine the mass of ethanol added.

3. Reassemble the freezing point apparatus in the warm water bath as before, and warm it enough to measure another cooling curve. The cooling bath temperature should be checked and more ice added if necessary.

4. Once the test tube of t-butanol and ethanol is in the cooling bath, stir and record the temperature every 15 seconds as before. Record the temperature and the time until the mixture has solidified. This time you will probably find that the mixture freezes in many small crystals rather than in one big mass.
   ⇒ Graph a new cooling curve for this mixture.

**Q 2:** What has happened to the freezing point?

5. Add another 0.40–0.50 grams of ethanol to the test tube. Be sure to record the actual mass of ethanol added to the test tube. After adjusting the heating and cooling baths, determine the freezing point of this second mixture.
   ⇒ Graph another cooling curve for this second mixture. In calculations be sure to use the combined masses of ethanol in determining the $K_f$ for this set of data.

   ***Note: One member of the pair should graph the data for the first addition, while the second person graphs the data for the second addition. Then share your results.***

**Calculations**

1. Determine the freezing point of the pure t-butanol from the graph as the temperature at which the slope of the curve changes. The two sets of data should agree.

2. Determine the freezing points of the two t-butanol–ethanol mixtures in a similar manner.

3. Calculate the molality of the two t-butanol–ethanol solutions. (Molality = number of moles solute per kg solvent.)
   ***Note: Use the mass of ethanol in the test tube for each set of measurements (not the amount added).***

4. Use the difference in freezing point between the pure solvent and the ethanol solution ($\Delta t$) and the molality of the solution ($m$) to calculate the molal freezing point depression constant, $K_f$, for each of the two ethanol–t-butanol solutions.

$$\Delta t = K_f \cdot m$$

**Q 3:** What is the average $K_f$ for the two additions of ethanol?

**Q 4:** Using your average $K_f$ value, how much ethanol should be added to each kilogram of t-butanol shipped to this Midwestern plant so that the mixture will remain fluid down to -10°F, as required?

**Q 5:** What is the purpose in doing two different measurements of the ethanol–t-butanol solutions with different amounts of ethanol added?

*GASOLINE ADDITIVE SCENARIO*
INSTRUCTOR NOTES

**Time Required**
The approximate time required to complete this activity in the lab, including a pre- and post-lab discussion, is 3 hours. During the post-lab, we had students construct their graphs which were used to determine the freezing point of each sample.

**Group Size**
Students can work individually or in pairs. We chose for students to work in pairs so that one student can watch the clock and record data while the other student stirs the solution and reads the temperature.

**Materials Needed**
per group:
- 150-mm test tube
- 2- or 3-hole rubber stopper to fit test tube
- thermometer that reads to 0.1°C (a digital thermometer works well)
- thermometer that reads to 1°C
- 100-mL beaker
- two 600-mL beakers
- metal or plastic stirrer with end pulled into a curve that fits around the thermometer yet is small enough to fit inside the test tube
- hot plate
- ice
- 30 mL pure t-butanol (not denatured)
- ethanol in a dropper bottle (each student needs 1.5 g, about 2 mL)

Note
✔ The t-butanol must be free of absorbed water. It is most convenient to use t-butanol that has not been previously opened. We have used unopened 500-mL bottles obtained from the supplier. Any t-butanol not used within a week is put aside for other purposes.

**Safety, Disposal, and Special Handling**
Review the Material Safety Data Sheets (MSDS) of any chemical used in the experiment for information regarding safety and handling. Dispose of any waste according to your local ordinances.

**Points to Cover in Pre-Lab**
- The purpose of this experiment is to have students use the procedures of freezing point lowering determinations to find the answer to the scenario question. You may need to review the basics of freezing point depression.

- You may want to remind students of the algebraic relationship between Celsius and Fahrenheit temperature scale or have them look it up.
- Remind the students about behavior around volatile liquids. It is important that students do not heat the t-butanol so long that they vaporize a significant amount. t-butanol has a pure freezing point of 25.6°C and a $K_f$ of 8.3°C/*m*. Thus, students need to heat their solutions to about 50°C, then cool in the water bath until freezing occurs. The water bath needs to be cold, but not so cold that the cooling occurs too quickly to follow. The procedure works, if followed as written.
- Show the students a set-up of the test tube, thermometer, stirrer, and two-hole stopper. Demonstrate stirring and point out that the stirring needs to be vigorous while minimizing the "splash" of the sample.
- If students work in pairs, one student can watch the clock and record data while the other stirs and reads the temperature. Make sure the students continue taking measurements even after the stirring rod is frozen in the t-butanol.
- Also, students can split up the calculations and graphs with one partner completing a graph for both Trial 1 and 3, and the other partner completing a graph for Trials 2 and 4. They can then exchange the information.

**Likely Play-Out of Lab**

The most common problem students have with Part I of the lab is stirring the solution vigorously, as demonstrated in pre-lab. The students should continue to collect several data points (2–3) after the t-butanol has frozen. This will make it easier to draw the leveling off point of the graph. Students should see a good leveling-off period on their cooling curve if the t-butanol is pure. We used new bottles of t-butanol to ensure this would happen. Once students graph their data, they should draw two straight lines, one through the original cooling points and one through the level points. The intersection point is considered the freezing point.

In Part II, where students add ethanol to the t-butanol, the experiment also works well. The biggest mistake students make is using the amount of ethanol added in Trial 2 for calculations instead of the total amount of ethanol in the test tube (approximately 1.1 g). In the mixtures, the level part of the cooling curve is never really seen. Thus, the graphing becomes even more important. Again, the two straight lines are drawn through the original cooling points and the points that have a distinctly different slope. It is suggested that you show students this method of interpreting graphed data. The slope of the level points should change significantly. The intersection of these two lines is considered the freezing point of the mixture.

**Possible Answers to Questions**

1. **A temperature change of 0.1°C corresponds to what size change in °F?**
   *A change of 0.1°C corresponds to a temperature change of 0.18°C.*

2. **What has happened to the freezing point?**
   *The freezing point will lower since there are more solute particles present. The more solute particles present, the more the freezing point of the solvent will be depressed. Assuming the use of 30 mL of t-butanol and 0.75 g of ethanol, the freezing point should lower approximately 5–6°C.*

3. **What is the average $K_f$ for the two additions of ethanol?**
   *t-Butanol has a $K_f$ of 8.3°C/m. The students' values will vary with technique, but should be in the range 8.0–8.6°C/m. Note: students sometimes forget to use the total amount of ethanol in the second mixture, which causes their calculations to be incorrect.*

4. **Using your average $K_f$ value, how much ethanol should be added to each kilogram of t-butanol shipped to this Midwestern plant so that the mixture will remain fluid down to -10°F as required?**
   *Assuming a $K_f$ of 8.3°C/m and a freezing point of pure t-butanol of 25.6°C, the company will need to use 268 g ethanol/kg t-butanol to keep the alcohol fluid at -10°F (-23°C).*

5. **What is the purpose in doing two different measurements of the ethanol/t-butanol solutions with different amounts of ethanol added?**
   *The purpose is to show that the lowering of the freezing point of a solvent is a function of the amount of solute added. The more solute, the lower the freezing point. However, the $K_f$ value will be the same (within experimental error) because it is a characteristic property of the solvent.*