THERMODYNAMIC PROPERTIES OF THERMAL STORAGE FLUIDS ALCOHOL-BASED APPLIED IN REFRIGERATION SYSTEMS WITH COOL THERMAL STORAGE

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Abstract. *This paper reports on a quantitative and comparative thermodynamic properties of water-alcohol(generic) solution as thermal energy storage fluid applied at indirect refrigeration systems. The analyzed properties are the melting point, density, specific heat and volumetric heat capacity, which are essential in the selection of the thermal fluid. Alcohol is used as antifreeze in the solution, because it alters the colligative properties of water and consequently the thermodynamic properties. Alcohols from renewable sources (ethanol and glycerol) and nonrenewable (ethylene glycol and propylene glycol) are used as antifreeze for the freezing point temperature of -17 °C, in the application range of -15 °C to 0 °C. The analysis shows that the lower the concentration of antifreeze, minor changes in the thermodynamic properties of the solution, especially ethanol as the best alcohol to reduce the melting point. For the entire temperature range, the density of water-glycerol solution is the highest among the studied solutions, and water-ethanol solution has the highest specific heat. Verifying volumetric heat capacity property, related to the able to the material to store thermal energy, ethanol proves to be the best antifreeze to thermal energy storage, and glycerol is worst alcohol, since this property is a relationship between the density and specific heat. Thus, for given concentrations of alcohols, water-ethanol solution has the best thermodynamic properties for thermal storage, keeping the qualities of its properties within the temperature range studied. Ethylene glycol, alcohol toxic widely used in cool thermal energy storage, is being replaced by propylene glycol, mainly because it is nontoxic and have good properties. The glycerol, co-product biodiesel production, shows low capacity as antifreeze, but can be feedstock for the production of propylene glycol, which is currently derived from non-renewable resources.*

Keywords*: Thermodynamic Properties, Cool Thermal Energy Storage, Alcohols, Renewable and Nonrenewable Resources.*

1. INTRODUCTION

Industrial applications of cool thermal energy storage for refrigeration and air conditioning systems use heat transfer fluids for thermal energy storage. Water has thermophysical properties that ensure its use as a thermal fluid. However, the applications of cool thermal storage, the fluids are cooled to temperatures lower than 0 °C, i.e., temperatures below the melting point of water.

The thermal storage fluids, in some cases cannot phase change, staying liquid even at temperatures below zero. Pure water freezes at 0 °C, which prevents its application in the cool thermal storage. The solution to this problem is to add antifreeze in the water.

Thermal storage fluids must have good thermodynamic and transport properties, and other factors such as being nontoxic, nonflammable, and chemically stable, with little or no corrosive activity (Dinçer, 2003; Stoecker, 1998). The main thermophysical properties involved in the selection are melting point, antifreeze concentration, density, specific heat, thermal conductivity and dynamic viscosity.

The antifreezes alter the thermophysical properties of water: there are changes in density, thermal conductivity and losses in specific heat, and increased dynamic viscosity (Ashrae, 2009, Melinder, 2007). These changes cause a lower thermal inertia, reduced ability to transfer heat and thermal energy storage, and increased pumping power.

The fluids consisting of water and alcohol (generic) are the most used. The brines were replaced by alcoholic solutions mainly by those present low or no corrosive activity, unlike the salts that are highly corrosive (Fink, 2003).

The alcohols used as antifreeze are methanol, ethanol, ethylene glycol, propylene glycol and glycerol (Ashrae, 2009; Melinder, 2007). The major toxicity of methanol combined with its high volatility and flammability with invisible flames dismiss its use as antifreeze. Currently, ethylene glycol is antifreeze most widely used, despite being toxic (Fink, 2003).

For the use of heat fluid as thermal energy storage, the thermodynamic properties should be satisfactory. Density, specific heat and volumetric heat capacity properties are analyzed. The main property is the specific heat, it is desirable that the fluid has a high this property for more efficient storage and reducing quantity in the storage tank (Carrier, 2003).

The selection of antifreeze is made from their data on their properties. Table 1 shows the thermodynamic properties of alcohols and water at 25 °C.

Thermodynamical Properties of Pure Alcohols and Pure Water at 25 °C

Alcohol	Melting Point (°C)	Molar Mass (kg/kmol)	Density (kg/m³)	Specific Heat (kJ/kg.K)	Volumetric Heat Capacity (MJ/m³.K)
Ethanol	-114,2	46	785	0,251	0,197
Glycerol	17,0	92	1261	0,241	0,304
Propylene Glycol	-59,0	76	1059	0,218	0,231
Ethylene Glycol	-10,8	62	1106	0,220	0,243
Water	0,0	18	997	4,179	4,166

Source: Dow Chemical, 2010a,b,c; Çengel, 2007

However, the properties of pure alcohol is not completely predict the behavior of water-alcohol solution, just give an orientation about. Table 2 presents data concerning alcohol-water solutions for the freezing temperature of -17 °C. This temperature is applied to cool thermal storage tank, in the working minimum temperature -15 °C.

Thermodynamical Properties of Solution Water + Alcohol at 20 °C

Solution Water +	Melting Point (°C)	Concentration (%)	Density (kg/m³)	Specific Heat (kJ/kg.K)	Volumetric Heat Capacity (MJ/m³.K)
Ethanol	-17,1	26,5	960	4,270	4,099
Glycerol	-17,1	42,5	1106	3,398	3,758
Propylene Glycol	-17,3	36,0	1029	3,827	3,938
Ethylene Glycol	-17,0	33,0	1043	3,669	3,827
Pure Water	0,0	0,0	998	4,182	4,174

Source: SecCool

Ethanol and glycerol are alcohols of renewable energy. The first is derived from fermenting vegetable carbohydrates (Cortez, 2010), and the second is from the manufacturing processes of soaps, fatty acids and biodiesel (Chun et al, 2007).

Propylene glycol and ethylene glycol are obtained from the petrochemical industry, from the hydration of propylene oxide and ethylene oxide, respectively, they are therefore non-renewable source. There is alternative route for production of propylene glycol, in which glycerol is subjected to the process of hydrogenolysis, making it come from renewable sources.

Thus, this study aims to examine, quantitative and comparative, thermodynamic properties of water-alcohol solutions as a thermal storage fluid, to check what is the best alcohol antifreeze, thus assisting in the selection process.

2. METHODOLOGY

Data on the thermophysical properties of the water-glycerol solution were obtained using SecCool, a program developed by the Department of Mechanical Engineering at the University of Denmark, which houses a library with the thermophysical properties of several secondary fluids, based mainly on experimental parameters of ASHRAE (American Society of Heating, Refrigeration and Air-Conditioning Engineers) and Ake Melinder, researcher in the Department of Energy Technologies of the Royal Institute of Technology of Sweden.

The solidification temperature is the same for all solutions: -17 °C. For this particular temperature, the concentration of each alcohol is function of its cryoscopic effect when in solution with water. The temperature range analyzed is from -15 °C to 0 °C.

The thermodynamic properties are analyzed antifreeze concentration, density, specific heat, and volumetric heat capacity, where the latter is a relationship between density and specific heat capacity that determines amount which this substance can store thermal energy.

Based on experimental data SecCool software, graphics have been made to show the thermodynamic behavior of each solution.

3. RESULTS AND DISCUSSIONS

3.1. Antifreeze Concentration

The concentration of alcohol in the solutions is due to the cryoscopic effect that each alcohol exerts when dissolved in water. All alcohols are infinitely soluble in water, which the reduction in melting point is determined mainly by intermolecular interactions between water and alcohol, where the molar mass of alcohol sets the amount of cryoscopic effect.

Observing Table 1, ethanol has a lower molar mass, and glycerol has a greater molar mass, among the alcohols examined. Table 2 shows that the higher the molar mass, less the effect of reducing the melting point, since the ethanol needs lowest concentration to solidify on temperature of -17 °C, and glycerol needs higher concentration (figure 1).

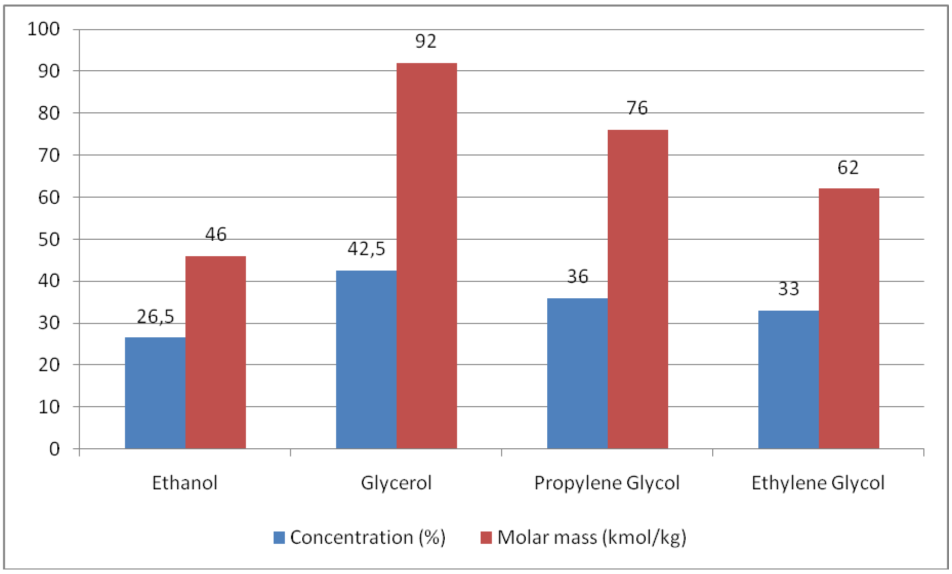

Figure 1 – Concentration the each alcohol as fuction of molar mass

This relationship between molar mass and lower melting point is related to the intermolecular interactions of the alcohol in water, that the closer the molar mass of alcohol, the more interactions are stronger.

Raoult's Law of the solutions shows that a decrease in the melting point of water (cryoscopic effect) is inversely proportional to the molar mass of the solute, and directly proportional to its concentration (Whitten et al, 2003). Thus, ethanol is alcohol more effective in reducing the melting point, and glycerol is the worst.

3.2. Density

Viewing the density data in tables 1 and 2, it finds that the density of water-alcohol solutions is related to the density of pure alcohol. Pure ethanol has a lower density of water, and glycerol has the highest density. The consequence of this is found in their solutions with water.

The density is not only related to the space occupied by the fluid to determine the size of the storage tank. It is also closely linked to the thermodynamic and transport properties of the solution. Volumetric heat capacity, thermal diffusivity and kinematic viscosity are examples of properties that are directly related to density (Incropera, 2006).

The associate values at density are function of temperature, which for most substances the lower the temperature, the higher the density. Exceptions to this rule is the pure water in the temperature between 0 °C and 4 °C and ice, where there is an expansion rather than contraction. In the item density versus temperature, all solutions behave as contraction upon cooling (Figure 2). The behavior of the curves is linear and smooth, showing no inflection points. The variations in density along each curve is minimal, less than 1% for all solutions in the range of temperatures analyzed.

The water-glycerol solution has the highest density, and water-ethanol solution the lowest. Due to the low density of pure ethanol, when in solution with water has lower density than pure water, damaging factor to the thermophysical properties of the solution. Ethylene glycol and propylene glycol have densities greater than that of pure water, creating dense solutions.

3.3. Specific Heat

One of the most relevant thermodynamic properties is specific heat. It is the amount of heat required to raise the unit mass of a substance by one degree Celsius (Çengel, Boles, 2006). The higher the specific heat of a substance, the more difficult it is to alter its temperature.

Although the specific heat value of substances is a direct function of temperature, the variations are slight and in some cases can be disregarded. Specific heat undergoes abrupt changes when a substance changes phase (Dossat, Horan, 2001).

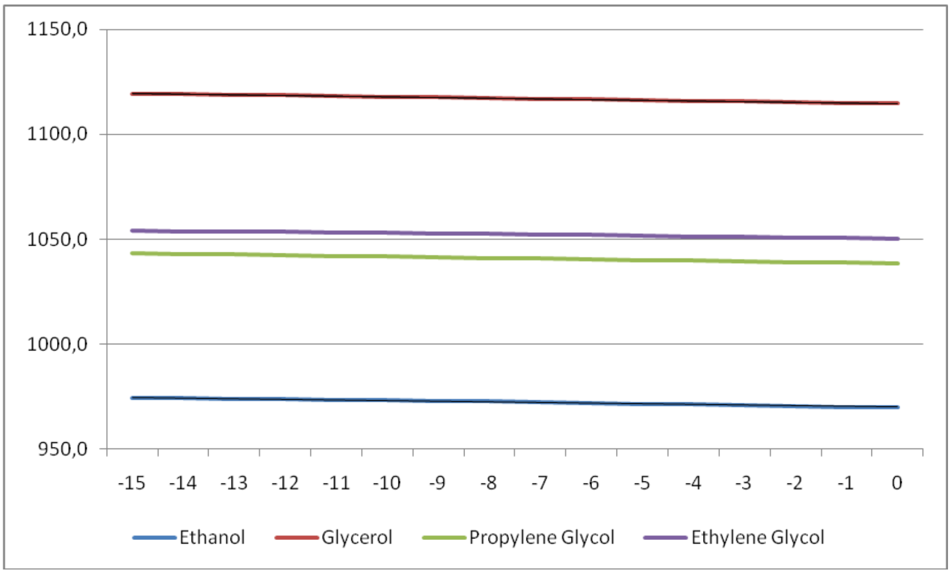

Figure 2 – Curves Density (kg/m³) versus Temperature (°C).

In the case of the solutions analyzed (Figure 3), only the propylene glycol-water solution shows negligible variations of specific heat, with variations of less than 0.1% can be considered constant over the temperatures examined.

All other solutions have small variations in the specific heat versus temperature, where the lower the temperature, the lower the property value. The water-glycerol solution has the highest percentage difference between extreme values of 2.5%, however, this value is negligible and the specific heat can be considered constant.

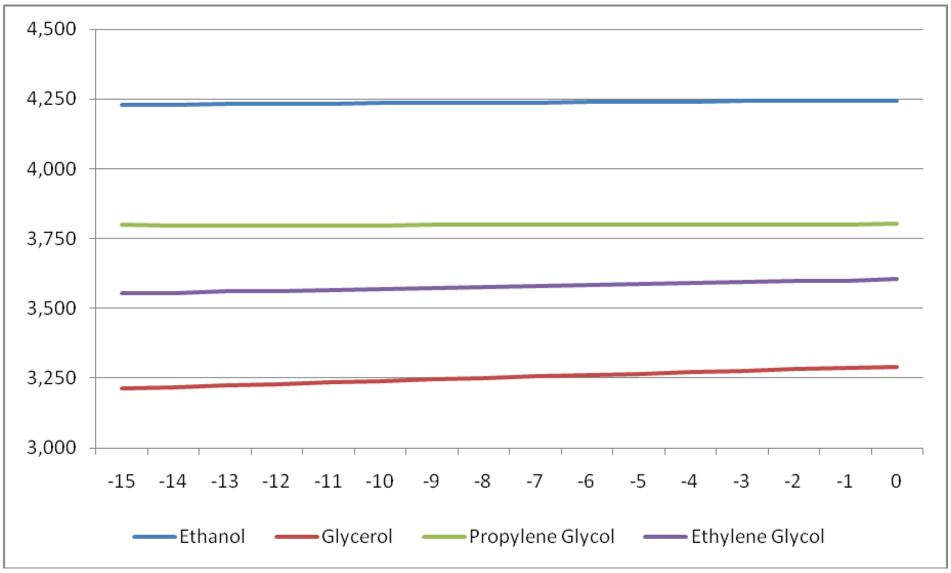

Figure 3 – Specific Heat (kJ/kg.K) as function of Temperature (°C).

Pure alcohols have specific heat far less than that of pure water (Table 1). The individual value of specific heat of alcohol each with its concentration does not predict the final value of the specific heat when in solution with water.

With the exception of ethanol-water solution, all the added alcohols reduced the specific heat of water (Table 2), confirming that the addition of antifreeze lowers the thermophysical properties of water. The specific heat of water-ethanol solution is relatively higher than that of pure water at 20 °C (Table 2), even at a temperature of -15 °C (Figure 3), unlike other solutions.

3.4. Volumetric Heat Capacity

Volumetric heat capacity (J/m³.K) is a relationship of thermodynamic properties density (kg/m³) and specific heat (J/kg.K). Both properties specific heat and volumetric heat capacity express the ability of the material to store heat (Çengel, 2007), i.e., the effect of thermal storage.

The density, on the other hand, is related to the mass of the molecules scattered in a unit volume. The higher the density, the greater the proximity of the molecules, and consequently, the more interactions and internal energy of the substance.

For applications in thermal energy storage, the volumetric heat capacity (VHC) is a thermodynamic property that best defines the fluid should be used. Analyzing this property for the pure fluids at 25 °C (Table 1), all pure alcohols do not accord the minimum specification for the retention of thermal energy energy, since for a fluid to be good for storing heat at its heat capacity volume must be greater than 1 MJ/m³.K (Incropera, 2006).

Water has excellent thermodynamic properties, except that freezes at 0 °C. The addition of antifreeze promotes the reduction of the melting point in detriment of the thermodynamic properties, except the ethanol.

For all the solutions described in Table 2, the ethanol-water solution has the highest volumetric heat capacity, whereas the glycerol-water solution has the lowest. Despite the low density of ethanol, the specific heat of solution is high enough to ensure that ethanol is the best additive, taking into account the volumetric heat capacity property. Glycerol, even with its high density, has the lowest specific heat among the solutions, which implies the lower VHC.

The graph in Figure 4, the curve of ethanol-water solution remains constant throughout the temperature range studied. The curve of propylene glycol shows an increase of the VHC according to the temperature is decreased, i.e., an inverse relationship. The curves of ethylene glycol and glycerol have a direct relationship between VHC and temperature, emphasizing the water-glycerol solution to a wide variation of VHC as a function of temperature.

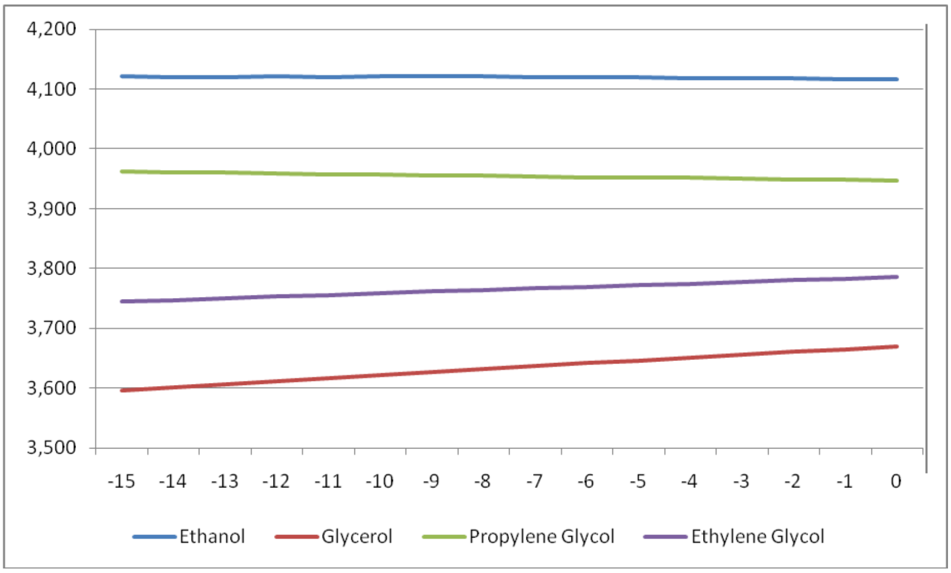

Figure 4 – Curves VHC (MJ/m³.K) versus Temperature (°C).

Variations of VHC with ethylene glycol and glycerol result in a decrease in the yield of thermal storage solutions when the temperature decreases; the ability to store heat also decreases, which implies a system of greater volume for these alcohols, when compared with the use of ethanol and propylene glycol.

4. CONCLUSIONS

The thermodynamic properties are essential in selecting a thermal storage fluid, considering not only the thermophysical properties of the additive, but also the behavior of water-alcohol solution.

Ethanol is surprisingly the alcohol more efficient to be used as antifreeze. For better interact with water, ethanol promotes a great cryoscopic effect in the solution, which allows to use low concentrations for the desired effect. Changes in the thermophysical properties that ethanol promotes is beneficial to the thermal storage, being upper to the other alcohols studied.

In addition to these major advantages, ethanol comes from renewable energy sources, favorable point for not damaging the environment and being ecologically correct. The major drawbacks in its use is that ethanol is corrosive and volatile, requiring the addition of corrosion inhibitors and a hermetic refrigeration system.

Propylene glycol shows its potential as a substitute for ethylene glycol in the cool thermal storage. It possesses properties that warrant its use without loss of energy efficiency in cool thermal energy storage, and is composed of a nontoxic, noncorrosive and non-volatile. Its biggest drawback is in the production process, that is from non-renewable sources of energy. However, this disadvantage can be overcome with the process feasibility of obtaining the propylene glycol from glycerin.

Ethylene glycol shows that its application as an additive in the cool thermal storage is not the best, and easily surpassed by its direct competitor, the propylene glycol. It presents reasonable properties for cool thermal storage, with the disadvantages of being toxic and from non-renewable sources.

The high density of glycerol is not sufficient to ensure a high volumetric heat capacity when in solution with water, showing the worst performance among the tested solutions, due to its lower specific heat. It is an alcohol derived from renewable, nontoxic, non-volatile and non-corrosive. Even with these advantages, its use as an antifreeze fluid for water heaters should be avoided.

5. ACKNOWLEDGMENTS

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6. REFERENCES

Ashrae, 2009, "Fundamentals Handbook". American Society of Heating, Refrigeration and Air Conditioning, Atlanta.

Carrier Air Conditioning Co., 2003, "Handbook of Air Conditioning System Design". McGraw-Hill, New York.

Çengel, Y. A., 2007, "Heat and Mass Transfer: A Practical Approach". 3rd edition. McGraw-Hill, New York.

Çengel, Y. A., Boles, M. A., 2006, "Thermodynamics: An Engineering Approach". 6th edition, McGraw-Hill, New York.

Chun, H. Z.; Beltramini, J. N.; Fan, Y. X.; Lu, G. Q., 2007, "Chemoselective catalytic conversion of glycerol as a biorenewable source to valuable commodity chemicals". Chemical Society Reviews, Australia, v. 37, n. 1, p. 527-549, nov. 2007.

Cortez, L.A.B., 2010, "Sugarcane Bioethanol". Edgard Blücher, São Paulo.

Dinçer, I., 2003, "Refrigeration Systems and Applications". John Wiley and Sons, West Sussex.

Dossat, R. J., Horan, T. J., 2001, Principles of Refrigeration. 5th edition. Prentice Hall, New Jersey.

Dow Chemical Co., 2010a, OPTIM Glycerine: physical properties. 10 March 2010. <http://www.dow.com/glycerine/resources/physicalprop.htm>

Dow Chemical, 2010b, "Propylene Glycol: Data Sheet". 20 Dec. 2010. < http://www.dow.com/propyleneglycol/products>

Dow Chemical, 2010c, "Ethylene Glycol: Physical Properties". 22 Dec. 2010. <http://www.dow.com/ethyleneglycol/about/properties.htm>

Fink, J. K., 2003, Oil Field Chemical. Gulf Professional Publishing, Burlington.

Incropera, F. P., et al, 2006, Fundamentals of Heat and Mass Transfer. 6th edition. John Wiley and Sons, Hoboken.

Knothe, G. et al (editors), 2005, The Biodiesel Handbook. AOCS Press, Champaign.

Medeiros, P. S. G., Barbosa, C. R. F., 2010, "Propriedades Termofísicas de Fluidos Secundários à Base de Álcool para Termoacumulação". Holos, Brazil, Year 26th, v. 4, p. 47-73, Nov. 2010.

Medeiros, P.S.G., Barbosa, C.R.F., Fontes, F.A.O., 2010, "Effects of Addition Glycerol Co-Product of Biodiesel in the Thermophysical Properties of Water-Glycerol Solution Applied As Secondary Coolant". 13th Brazilian Congress of Thermal Sciences and Engineering. ABCM, São Paulo.

Melinder, A., 2007, Thermophysical "Properties of Aqueous Solution Used as Secondary Working Fluids". Doctoral Thesis, Royal Institute of Technology, Stockholm.

Silberberg, M. S., 2007, "Principles of General Chemistry". McGraw-Hill. New York.

Solomons, T. W. G., Fryhle, C., 2007, "Organic Chemistry". 9th edition. John Wiley and Sons, Hoboken.

Stoecker, W. F., 1998, "Industrial Refrigeration Handbook". McGraw-Hill, New York.

Whitten, K. W., et al., 2003, "General Chemistry". 7th edition. Brooks Cole.

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