國立雲林科技大學
九十三學年度博士班招生入學考試試題

所別：化學工程系
科目：化工熱力學

1. **(a)** Derive the expression for dS as a function of T and P for any fluid by using the Maxwell relations. （10%）

   (b) If the Gibbs energy varies with temperature according to

   $$G/T = a = b/T + c/T^2$$

   How will the enthalpy and entropy vary with temperature? （10%）

2. **(a)** Steam is condensed at 100℃ and the water is cooled to 0℃ and frozen to ice. What is the molar entropy change of the water? Consider that the average specific heat of liquid water is 4.2 $JK^{-1}g^{-1}$. The heat of vaporization at the boiling point and the heat of fusion at the freezing point are 2258.1 and 333.5 Jg^{-1}, respectively. （15%）

   (b) Calculate the change in molar entropy of aluminum which is heated from 600℃ to 700℃. The melting point of aluminum is 660℃, the heat of fusion is 393 Jg^{-1}, and the heat capacities of the solid and liquid may be taken as 31.8 and 34.3 $JK^{-1}mol^{-1}$, respectively. (15%)

3. (25%)

Equilibrium data are needed for you to design an absorber to remove acetone vapor from an air stream using water as a solvent. The equilibrium data for the acetone-water system are tabulated as follows.

x_A	0.0194	0.0289	0.0449	0.0556	0.0939
y_A	0.5234	0.6212	0.7168	0.7591	0.8351
P (mmHg)	50.1	61.8	81.3	91.9	126.1

At 25°C, the vapor pressures of acetone and water are:

$$P_A^o = 230.05\,\text{mmHg}$$

$$P_W^o = 23.76\,\text{mmHg}$$

(a) Determine a thermodynamic parameter best to describe the behavior of acetone in water at above various compositions? (10%)

(b) If the absorber is operated at 1 atm, determine the mole fractions of acetone in air which are in equilibrium with mole fractions of acetone in water at above various compositions and at 25°C. (15%)

4. (25%)

Chemical vapor deposition at different pressures is a well known method to prepare carbon film materials on substrates. Mixtures of CO and CO_2 are to be processed at temperatures between 900 and 1000 K. It is desired to know what conditions solid carbon might deposit according to the reaction

$$CO_2(g) + C(c) = 2CO(g)$$

For this reaction the equilibrium constants are

T(K)	K
900	0.178
1000	1.58

Please comment on the process feasibility with CO mole fractions in the temperature range of 900-1000 K and at pressures of 1 and 10 atm ?

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一共兩大題，每題50分。

一、 針對「附件一」內容，請回答以下問題。

1-1、 以中文製作本文的摘要。

1-2、 請將文章第1及第3段內容翻譯成中文。

1-3、 添加酒精於汽油中，有何優缺點？何謂GASOHOL？

1-4、 MTBE之使用近年成為爭論之話題，請申論之。

二、 針對「附件二」內容，請回答以下問題。

2-1、 請簡述附件二之大意為何？

2-2、 請將文章第2段內容翻譯成中文。

2-3、 根據文章內容之說法，此技術（材料）開發成功之後，可當作什麼之用？

2-4、 請針對此技術給予評論及討論。

(附件一)

Oxygenated Gasoline

In response to the Clean Air Act of 1992, the composition of gasoline is being changed as a means of improving air quality. Beginning in November, 1992, all gasoline sold during the winter months—November through February—in 39 designated areas of the United State, must contain 2.7 percent oxygen. The thirty-nine areas represent the most densely populated regions in the country and include most major metropolitan areas (New York, Washington, Chicago, etc.). These areas have been shown by the EPA to have carbon monoxide (CO) concentrations that exceed the federally mandated ceiling during the winter. In rural areas CO levels average under 10 ppm, but in areas of heavy traffic, CO levels can rise as high as 100 ppm. Poorly ventilated tunnels and parking garages are especially dangerous.

Because the automobile engine is the primary source of carbon monoxide emission, regulation of tailpipe emissions should improve air quality. Carbon monoxide emission can be lowered by using a leaner air-fuel mixture, that is, one in which there is greater than 16 to 1, CO emissions are greater reduced. This air to fuel ratio, however, is impractical, because if the engine is tuned this "lean" it is difficult to start and may stall while idling. This is especially true in winter when the engine is cold and harder to start and the fuel does not vaporize as easily. Catalytic converters also cut down on CO emissions; air pumped into the exhaust system facilitates the oxidation of CO to CO_2. The addition of ethanol to gasoline is another method of oxygenation.

Brazil has been a leader in the use of ethanol as an automotive fuel, producing more than 4 billion liters per year. At one time, Brazil had more than 450000 cars running on pure ethanol. The carburetor or fuel injection system of an automobile has to be modified to use pure alcohol. As petroleum prices fell in the 1980s, many of these cars were converted back to gasoline. Brazil's interest in ethanol production stems from the fact that the country has few petroleum reserves, but has a huge sugarcane industry producing biomass.

The octane rating of ethanol (108) is higher than that of isooctane (100). Thus, a mixture of gasoline and ethanol has a higher octane rating than regular gasoline. The addition of alcohol also reduces exhaust emissions of CO by as much as 50 percent. Gasoline blended with up to 20 percent ethanol was named gasoline when it was introduced in the 1970s. This mixture, unlike pure alcohol, can be used without any modification of the automobile engine.

Ethanol can be produced by fermentation of carbohydrates from waste agricultural material. The cost of production, however, is higher than that of gasoline, and farmers are lobbying for government support for the creation of an alcohol

(附件一)

industry to provide fuel for automobiles. Because it is formed from plant material, alcohol may be considered a renewable resource rather than a depletable fossil fuel, and the fermentation of waste products is a method of recycling.

At present, most U.S. petroleum companies are increasing the oxygen content of their gasoline, not by adding alcohol, but by adding methyl-t-butyl ether (MTBE). The oxygen content of gasoline is increased to 2.7 percent if the concentration of MTBE is set at 15 percent. This use of MTBE necessitates the production of hung quantities of the chemical, and since 1990, MTBE has been on the list of the top 25 industrial chemicals produced in the U.S.

U.S. petroleum companies are choosing MTBE instead of ethanol for two reasons. First, MTBE has an octane rating of 116, which is higher than that of ethanol, and as a result, gasoline formulated with MTBE runs more smoothly and "knocks" less. Second, MTBE does not evaporate as quickly as does ethanol, so it does not vaporize out of the gas tank and add to evaporative emissions.

Although oxygenated gasoline reduces the emission of CO from automobiles, consumers have two complaints about the fuel：gasoline formulated with MTBE costs 5 to 10 cents more than regular gasoline and mileage is reduced by 10 percent.

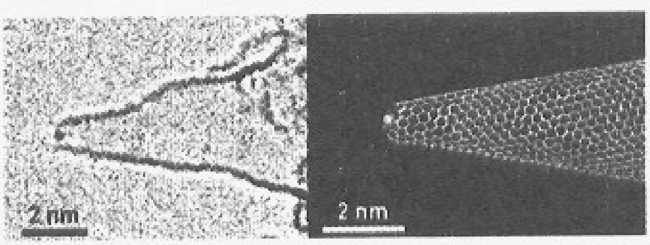
（附件二）

SHIP IN A BOTTLE

Metal clusters are grown inside a nanohorn through a hole in its side

It's not just because carbon nanotubes usually are empty that researchers try to trap atoms or molecules inside them. Scientists suspect that nanotubes filled with metal atoms could have promising applications as catalysts and semiconductors. Now, a research group in Japan has devised a method to precisely control the size and location of metal clusters within a single-walled carbon nanohorn--a megaphone-shaped type of nanotube [*Proc. Natl. Acad. Sci. USA,* **101,** 8527 (2004)]. University of Tokyo chemistry professor Eiichi Nakamura and Sumio Iijima of NEC Corp. and Japan's Research Center for Advanced Carbon Materials spearheaded the research.

To construct the metal-encapsulated structures, the group begins by heating the nanohorns at 420 to 580 °C in the presence of O_2. Under these conditions, the nanohorns become pierced and the edges of the new openings are oxidized, creating small regions of hydrophilicity in the hydrophobic graphene structure. When the perforated nanohorns are placed in a methanolic solution with $Gd(OAc)_3 \cdot (H_2O)_4$, the hydrophilic Gd(III) ions accumulate one by one at the oxidized openings. The researchers expect that other metal ions will behave in a similar fashion. By observing this process, they conclude that the size and location of the opening ultimately determine how many metal ions will aggregate there and whether they will be encapsulated by the tube.



SEEING SPOTS TEM image and corresponding model of a Gd atom (blue) lodged at the oxidized tip of a nanohorn. PNAS/COURTESY OF EIICHI NAKAMURA

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（附件二）

"Thanks to the availability of the first scanning transmission electron microscope (STEM) capable of performing high-resolution electron energy loss spectrometry for a 3- ×3-Å area, we could identify, for the first time, metals trapped within the graphene wall or within the interior of the nanohorn," Nakamura says.

The group noted that metal ions won't travel through openings at the tapered tips of a nanohorn, but instead, a lone atom can become lodged there. However, metal clusters will form inside the structure if the opening is in the nanohorn's side. There, a cluster of metal ions will develop inside the tube until the aggregate extends to the internal hydrophobic wall opposite the opening. The researchers call the technique a "ship-in-bottle" synthesis.

"The impact of such a technique lies in our ability to control defect dynamics in nanotube structures and hence controllably create hybrid nanotube-based structures," comments Pulickel M. Ajayan, a materials engineering professor at Rensselaer Polytechnic Institute, Troy, N.Y. He describes the report as "a very nice demonstration of how in situ microscopy can be used to reveal real-time events and follow the dynamics of reactions, defect creation, and encapsulation. Kudos go to the masterly microscopy and amazingly clear images."

Chemical & Engineering News, 2004.