



TMT4320 Nanomaterials, fall 2015

EXERCISE 5 - SOLUTION

PROBLEM 1

- a) A supercritical (sc) fluid is a fluid that has been heated in a closed vessel to reach a temperature and pressure above the critical pressure and temperature, the critical point, for that specific fluid. The critical point is the end point of the liquid-vapor coexistence curve in the P vs T phase diagram. A fluid in this state is neither a gas nor a liquid and has properties intermediate between the gas and the liquid for this compound.

The viscosity of a sc fluid is higher than that for the gas and 10 to 100 times lower than the value for the liquid. The viscosity is also highly dependent on both T and P and shows a rapid increase as a function of P above the critical point. Since the diffusion of a solute in a sc is highly dependent on the viscosity, the diffusion will show similar properties to the viscosity, and the diffusivity increases with increasing temperature and decreasing pressure.

The dissolving power of a sc fluid, which is related to the solubility, is directly proportional to T and P. The dissolving power increases when the pressure increases and when the density increases which leads to an increase in the solubility. For many substances, sc fluids have much better dissolving power than gases and liquids and are therefore used extensively in industrial processes.

- b) Some applications of sc fluids include petrochemical and pharmaceutical industry, cosmetics, extraction of the bitter component from hops in the brewing industry and caffeine from coffee beans.
- c) The process used to synthesize nanoparticles using supercritical fluids is called rapid expansion of a supercritical solution (RESS). The first step in implementing this procedure is to solubilize the solute (metal compound or other precursor) in the supercritical fluid phase. The next step is to depressurize the SCF solution, leading to a sudden drop in solubility. This favors super-saturation of the solute and formation of a particle precipitate (metal, molecular cluster, etc.).
Nucleation and growth during the expansion are determining factors in the morphology of the final deposit. It is important to remember here that it is not a change in concentration that brings the mixture into the supersaturated state, but a change in solubility. Dilute solutions favor the formation of a thin film of the solute, while concentrated solutions favor nucleation and growth and particle powders are obtained.
- d) Supercritical fluids can be used in both physical and chemical procedures. Explain the difference between these two. Physical procedures involve the use of the RESS process and variations in the physical parameters initiates the wanted processes. There is no chemical reaction involved to obtain the end product. Chemical procedures make use of chemical reactions and do not require an expansion of the liquid for the reaction to take

place. The supercritical fluid is here often used to control diffusion and thereby growth rates, or it can be used to control size of the particles by other means (i.e. controls water content in reverse micelles). Using a supercritical fluid may also enable use of precursors that otherwise would not be possible in a regular liquid or gas.

- e) When using sc fluids in combination with micelles, for reasons of solubility, the hydrocarbon chain is replaced by a fluorocarbon chain in the case of CO₂ or other chains which ensure solubility in the supercritical fluid. The size of micelle is also here related to [H₂O]/[SA], but it is also possible to use pressure to control the amount of water inside the reverse micelle. Increased pressure → increased amount of water in the micelle → increased size of micelle. In addition, diffusion-limited reactions are more rapidly achieved for micelles in a supercritical fluid. And it is possible to reach high temperature while maintaining a degree of stability of the micelle system.

PROBLEM 2

a)
$$n_{\text{H}_2\text{O}} = \frac{m}{M} = \frac{\delta \cdot V}{M} = \frac{1.0 \text{ g/mL} \cdot 50 \text{ mL}}{18.016 \text{ g/mol}} = 2.775 \text{ mol}$$

$$V = V_m \cdot n = 24.46554 \text{ L/mol} \cdot 2.775 \text{ mol} = 67.89 \text{ L} \approx 68 \text{ L}$$

b)
$$P = \frac{nRT}{V} = \frac{2.775 \text{ mol} \cdot 8.314510 \text{ J K}^{-1} \text{ mol}^{-1} \cdot 453 \text{ K}}{125 \times 10^{-6} \text{ m}^3} = 8.36 \times 10^7 \text{ Pa} = 836 \text{ bar}$$

Remember that: $\frac{\text{J}}{\text{m}^3} = \frac{\text{Nm}}{\text{m}^3} = \text{Pa} = 10^{-5} \text{ bar}$

- c) The autogenerated pressure is lower than calculated in b) because all the water is *not* in the gas state. Most of the water will be in a liquid state. The conditions approach the critical point of water (374.1 °C, 22.1 bar) but the system will consist of both gas and liquid at 180 °C.
- d) Some general guidelines for controlling the synthesis of nanoparticles in hydrothermal/solvothermal synthesis:
- pH can be used to control crystal structure
 - Temperature can control dispersity (size distribution)
 - Concentration can be used to control phase purity or mixed phases → higher concentration often gives higher phase purity
 - Capping agents may be necessary to control growth and/or prevent aggregation
 - Particle size can also be controlled by reaction time and/or addition of amines, surfactants and ions
 - Mineralizers can be added to reduce grain size, but may also cause agglomeration.
- e) Particle growth can be monitored in situ in hydrothermal/solvothermal synthesis. However, “normal” autoclaves cannot be used for this purpose. The autoclave can be replaced by a sapphire vial, and the furnace or heating cabinet normally used to heat the autoclave is replaced by heating coils. The sapphire is strong enough to withstand the pressure and temperatures necessary for the synthesis to proceed, while at the same time being transparent to x-rays. Using x-ray diffraction analysis, phase purity and evolution of different phases as well as particle size and particle growth can be analyzed.