

Chemical Engineering Thermodynamics
Quiz 8
March 7, 2019

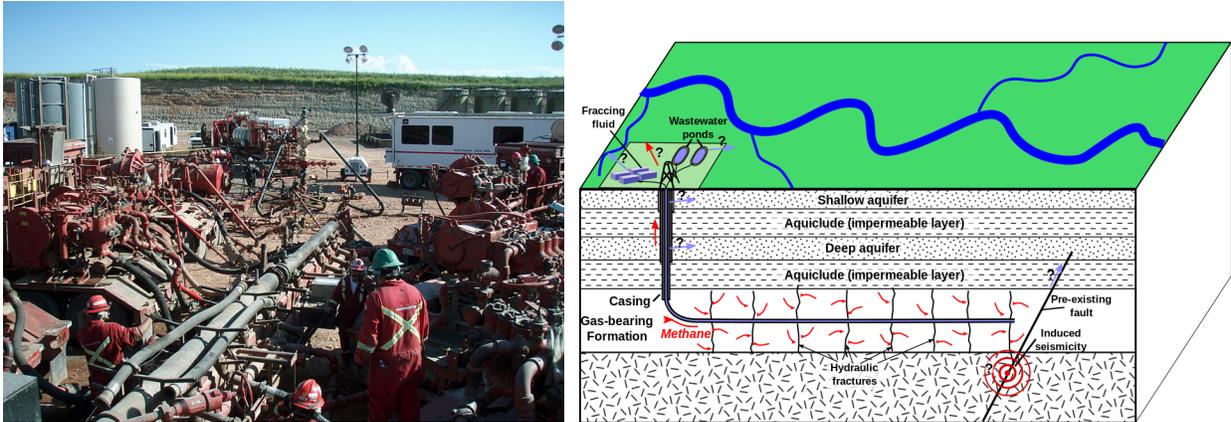


Figure 1. a) Hydraulic fracturing operation at the surface. b) Profile of fracking operation. c) Simulated pressure profile showing an initial explosion/earthquake spike followed by an exponential decay. (x-axis linear-scale 0 to 20 MPa; y-axis 0 to about 1 hour (3000 s).)

Hydraulic fracturing involves pumping an aqueous solution into into a deep rock formation using a gas or oil well at 1 MPa followed by an explosive spike in pressure up to 150 MPa to open the cracks in the rocks followed by injection of fine sand to wedge the cracks open. High pressure is necessary to overcome the weight of the rocks and force the fluid into the pores but once water occupies the pores Young-Laplace capillary pressures act to pulverize the bed rock. The figure above shows the pressure/time profile for a simulated fracking operation. Natural gas (methane) leaks through the cracks to a well head. The method has been used since the 1940's but is expensive and not particularly predictable so it hasn't been widely used until the recent rise in crude oil and natural gas prices which made the method economical. Of the 2 million oil and gas wells in the US, 70% are fracked wells.

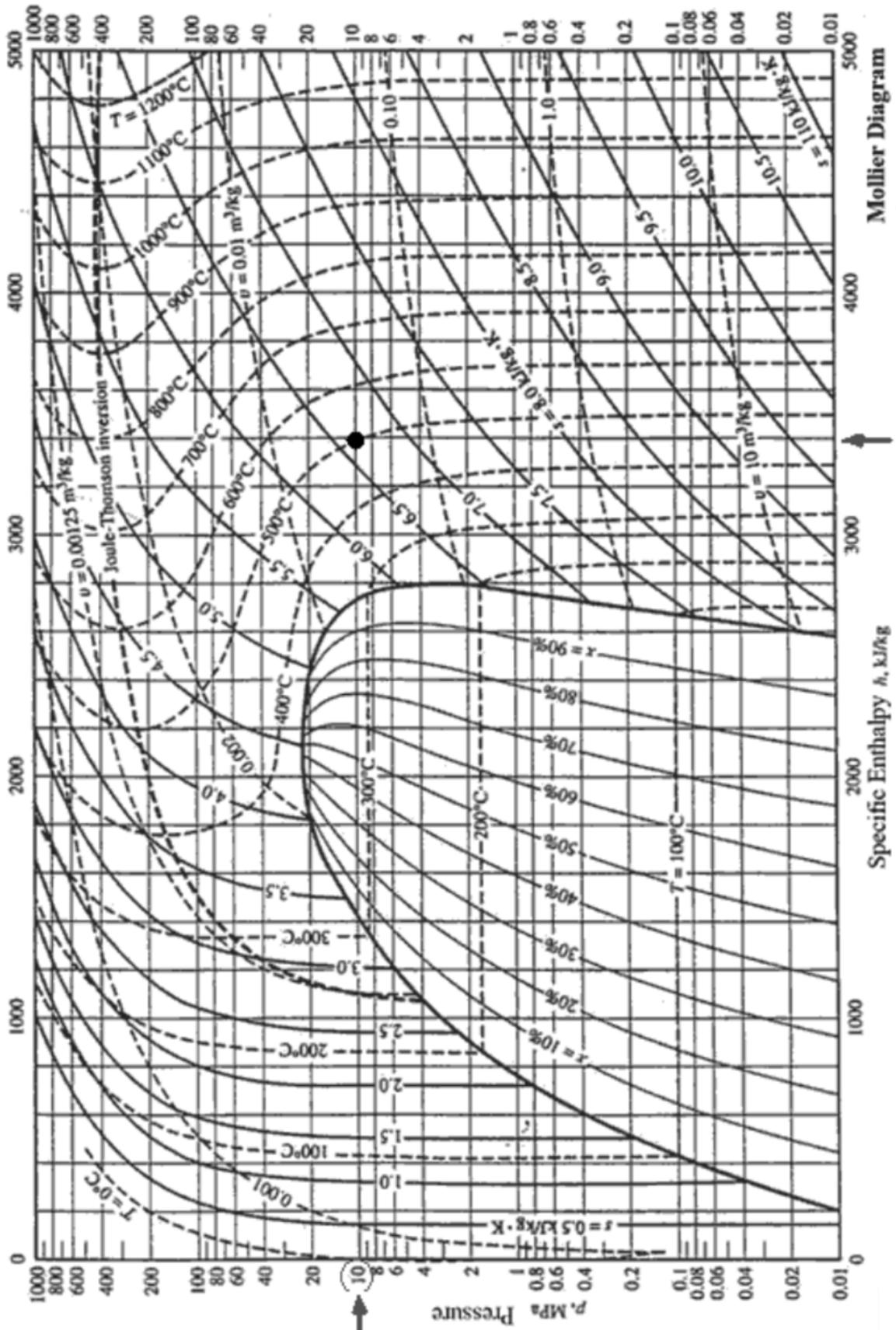
Use your computer and the PREOS.xls file to calculate properties for this quiz, using 298°K and 0.1 MPa as the reference state. (The pressure enthalpy charts for water and methane are provided only for reference do not use these to get values.)

PLEASE PUT ALL ANSWERS FOR a-e IN THE TABLE. T_c and P_c are listed in the table. For the reference state choose a real fluid; $H_R = 0$; 298°K; and 0.1 MPa.

- a) Use PREOS.xls to fill in the missing parameters in the table below for water at the injection pressure and temperature. (The pressure enthalpy chart for water is provided for reference but not to answer the questions; Use 298°K and 0.1 MPa as the reference state.)
- b) The explosion at the start of fracking occurs adiabatically and reversibly. Assume the fracking fluid is pure water. Use Solver® to fill in the second row of missing parameters in the chart. Use PREOS.xls. (Use solver to vary the temperature and find the desired entropy in PREOS.xls.)
- c) Water in the pores of the shale is subject to pressure associated with the small pore size (about 5 nm radius). The Young-Laplace Equation for droplets or pores is $\Delta P = 2\gamma/R$. From the Laplace equation, the pressure difference between the 10 MPa fluid (at the end of the decay curve above) and the internal pore is: $\Delta P = 25$ MPa. Assume the pressure decay is isenthalpic like a throttle from the peak of the explosion. Fill in the table for the state of water in the pores at the end of the decay in pressure (use solver).
- d) At the peak of the explosion what is the state of methane? Use the T and P from water in part “b”. Fill in the first row for methane in the table. (Reference state 298°K and 0.1 MPa.)
- e) About 10% of the “fracked” methane (a potent greenhouse gas) escapes into the atmosphere. If the leakage is isenthalpic, like a throttle, what are the properties of the methane when it reaches 0.1 MPa? Use initial condition in the pores from part “c” for T_i and P_i and use Solver similar to problem “b”. (Use 298°K and 0.1 MPa real fluid as the reference state.)
- f) *Extra Credit:* Will methane display a similar Young-Laplace pressure in the pores?
- g) *Extra Credit:* If we assumed the change in enthalpy for part “b” was $V\Delta P$ would you get an equivalent change in enthalpy? Why are the values different?

Stage	State*	T, °K	P, MPa	V, cm ³ /mol	Z	H, J/kmol	S, J/(mol °K)	ΔH, J/mol
WATER $T_c = 647$ °K; $P_c = 22.1$ MPa								
a) Injection	L	298	1					
b) Peak of Pressure			101					
c) Young-Laplace Pressure			35					
METHANE $T_c = 191$ °K; $P_c = 4.60$ MPa								
d) Peak of Explosion			101					
e) Young-Laplace Water P/T			35					
e) Atm. Pressure			0.1					

*Possible States: CL Compressible Liquid $P > P_c$, $T < T_c$; SCF Super Critical Fluid $P > P_c$, $T > T_c$; IG Ideal Gas $1.05 > Z > 0.95$; L/V Liquid Vapor in Equilibrium; L Liquid; V Vapor

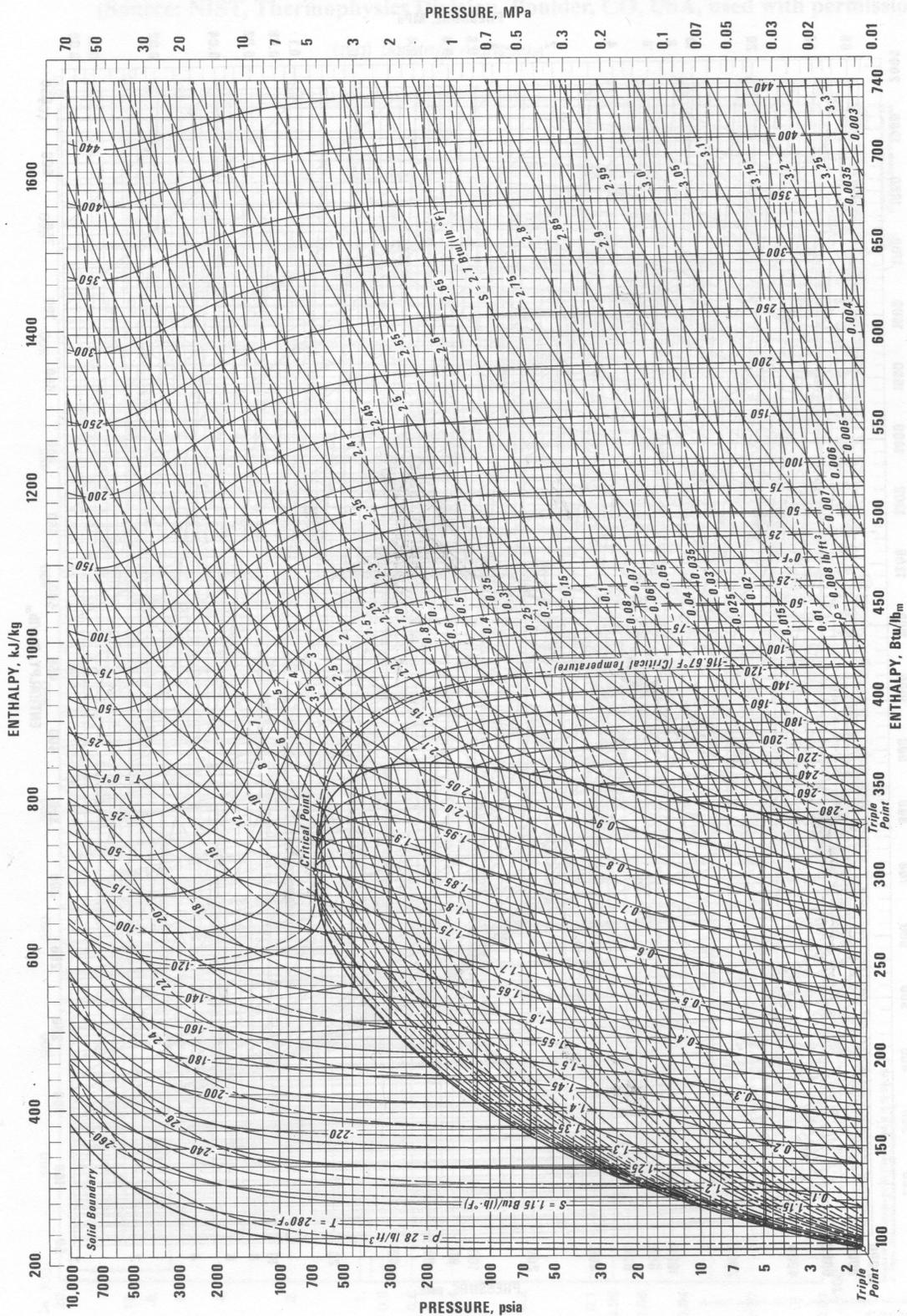


Mollier Diagram

Specific Enthalpy h , kJ/kg

E.10 PRESSURE-ENTHALPY DIAGRAM FOR METHANE

(Source: NIST, Thermophysics Division, Boulder, CO, USA, used with permission.)



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ANSWERS:
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Stage	State*	$T, ^\circ\text{K}$	P, MPa	$V, \text{cm}^3/\text{mol}$	Z	$H, \text{J/kmol}$	$S, \text{J}/(\text{mol } ^\circ\text{K})$	$\Delta H, \text{J/mol}$
WATER $T_c = 647 ^\circ\text{K}; P_c = 22.1 \text{ MPa}$								
a) Injection	<i>L</i>	298	1	21.2	0.0085	15.3	-0.0125	--
b) Peak of Pressure	<i>CL</i>	303	101	21.0	0.843	2120	-0.0125	2100
c) Young-Laplace Pressure	<i>CL</i>	317	35	21.3	0.284	2120	4.48	0
METHANE $T_c = 191 ^\circ\text{K}; P_c = 4.60 \text{ MPa}$								
d) Peak of Explosion	<i>SCF</i>	303	101	42.4	1.70	-3090	-66.7	--
e) Young-Laplace Water P/T	<i>SCF</i>	317	35	71.6	0.951	-2720	-54.5	370
e) Atm. Pressure	<i>IG</i>	217	0.1	17900	0.994	-2720	-10.6	0

*Possible States: *CL* Compressible Liquid $P > P_c, T < T_c$; *SCF* Super Critical Fluid $P > P_c, T > T_c$; *IG* Ideal Gas $1.05 > Z > 0.95$; *L/V* Liquid Vapor in Equilibrium; *L* Liquid; *V* Vapor

f) Methane is a super critical fluid so it does not display surface tension. Hence there is no Laplace pressure generated ($\gamma_{\text{methane}} = 0$ under these conditions).

g) $100\text{MPa } 1\text{cm}^3/\text{g} = 100 \text{ J/g}$
 $100\text{J/g } 18 \text{ g/mole} = \mathbf{1800 \text{ J/mole}}$

The tabulated value is 2100 J/mole. A 20% difference. The fluid isn't incompressible at these pressures. At 101 MPa water is a compressible liquid so the specific volume isn't constant. $360\text{J/mol}/1800\text{J/mol}$ gives a 20% change.

	liquid water	liquid methane
density	1 g/cc	0.45 g/cc
surface tension	70 dyne/cm	17 dyne/cm (e-7 J/cm2)
viscosity	1.54 cP	0.184 cP

and for Methane filled pores ($\gamma = 1.7 \text{ e-6 J/cm}^2$; $P = 17\text{MPa}$). for pure methane liquid surface tension at 200K is 6e-8J/cm^2 .

($\gamma_{\text{methane}} = 1.7 \text{ e-6 J/cm}^2$)