CH365 Chemical Engineering Thermodynamics

Lesson 31
Two-Phase Systems, Thermodynamic Diagrams,
and Property Tables

Lessons 28-30 Recap

- Mathematics from Maxwell leads directly to Gibbs energy generating functions.

- Gibbs energy generating functions lead directly to residual properties G^R, H^R, and S^R and a recipe to calculate them.

- Residual properties G^R, H^R, and S^R add to ideal gas properties G^{ig}, H^{ig}, and S^{ig} to generate real properties G, H, and S.

- Generalized methods – Lee-Kesler Tables and Virial Equation that are somewhat simpler less accurate.

Today's Agenda

- Vapor-liquid phase equilibrium.

- Origin of the "Antoine equation."

$$\ln P^{sat} = A - \frac{B}{T + C}$$ (Eq. 6.76)
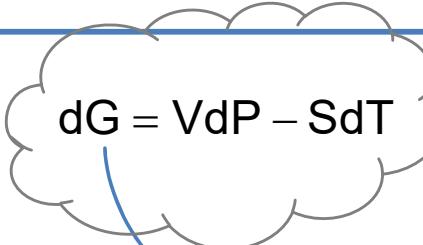
A, B, and C are constants in Table B.2 on page 682

P^{sat} is vapor pressure in kPa and T is temperature in °C

Used in flash and distillation calculations – enables Raoult's Law calculations

Fundamental Property Relations

**Property relations for a homogenous fluid of constant composition:**
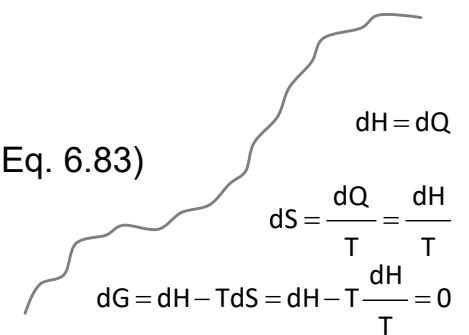
$dU = TdS - PdV$ (Eq.6.8)	$dH = TdS + VdP$ (Eq. 6.9)
$dA = -PdV - SdT$ (Eq. 6.10)	$dG = VdP - SdT$ (Eq. 6.11)

- Equilibrium is the absence of change
- Postulate that Gibbs energy is the "driving force" for phase change

- Consider a closed 2-phase system.
- Phases α and β - <u>system is α plus β</u>
- Constant T and P.

- It follows that the Gibbs energy in each phase is equal. A *fundamental condition* for equilibrium is that $G^\alpha = G^\beta$

$dG = 0$ for the system $\alpha + \beta$

$$dG^\alpha = dG^\beta$$

$$G^\alpha = G^\beta \quad \text{(Eq. 6.83)}$$

$$dH = dQ$$

$$dS = \frac{dQ}{T} = \frac{dH}{T}$$

$$dG = dH - TdS = dH - T\frac{dH}{T} = 0$$

A vapor initially in equilibrium with its liquid undergoes a differential amount of evaporation.

$$dG = VdP - SdT$$

$$\boxed{dG^{\alpha} = dG^{\beta}}$$

(Eq. 6.11)

$$V^{\alpha}dP - S^{\alpha}dT = V^{\beta}dP - S^{\beta}dT$$

For a differential amount of evaporation, dP and dT approach zero but are not zero

$$V^{\alpha}dP^{sat} - S^{\alpha}dT = V^{\beta}dP^{sat} - S^{\beta}dT$$

At equilibrium P = P^{sat}

$$V^{\alpha}dP^{sat} - V^{\beta}dP^{sat} = S^{\alpha}dT - S^{\beta}dT$$

$$\left(V^{\alpha} - V^{\beta}\right)dP^{sat} = \left(S^{\alpha} - S^{\beta}\right)dT$$

$$\frac{dP^{sat}}{dT} = \frac{S^{\alpha} - S^{\beta}}{V^{\alpha} - V^{\beta}} = \frac{\Delta S^{\alpha\beta}}{\Delta V^{\alpha\beta}}$$

Benoit Clapeyron, 1799-1864
(image from Wikipedia)

$$dH = TdS + VdP$$

(Eq. 6.9)

Consider for transition from α to β
Integrate at constant T and P
(pressure term goes away).

$$\Delta H^{\alpha\beta} = T\Delta S^{\alpha\beta} \quad \text{(Eq. 6.84)}$$
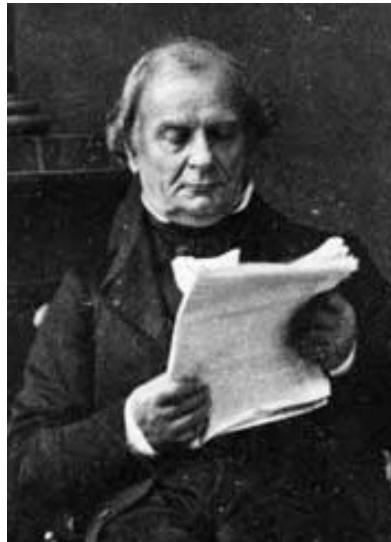
$$\Delta S^{\alpha\beta} = \frac{\Delta H^{\alpha\beta}}{T} \quad \text{(Eq. 6.84)}$$

$$\frac{dP^{sat}}{dT} = \frac{\Delta S^{\alpha\beta}}{\Delta V^{\alpha\beta}} = \frac{\Delta H^{\alpha\beta}}{T\Delta V^{\alpha\beta}}$$

Clapeyron Equation
(basis for phase change enthalpy calculations)

(Eq. 6.85)

Transition from liquid l to vapor v
(change labels α and β to l and v)

$$\frac{dP^{sat}}{dT} = \frac{\Delta H^{\alpha\beta}}{T\Delta V^{\alpha\beta}} \quad \Rightarrow \quad \frac{dP^{sat}}{dT} = \frac{\Delta H^{lv}}{T\Delta V^{lv}} \qquad \text{(Eq. 6.86)}$$

$$Z \equiv \frac{PV}{RT} \quad \Rightarrow \quad \Delta Z^{lv} = \frac{P^{sat}\Delta V^{lv}}{RT} \quad \Rightarrow \quad \Delta V^{lv} = \frac{RT}{P^{sat}}\Delta Z^{lv} \qquad \Delta Z^{lv} = \text{change in Z on vaporization}$$

(from roots of cubic EOS)

(P^{sat} and T are constant in
phase change equilibrium)

$$\frac{dP^{sat}}{dT} = \frac{P^{sat}\Delta H^{lv}}{RT^2\Delta Z^{lv}}$$

$$\frac{dP^{sat}}{dT}\frac{1}{P^{sat}} = \frac{\Delta H^{lv}}{RT^2\Delta Z^{lv}}$$

$$\frac{1}{P^{sat}}dP^{sat} = d\ln P^{sat}$$

$$d(1/T) = -\frac{1}{T^2}dT$$

$$\frac{d\ln P^{sat}}{dT} = \frac{\Delta H^{lv}}{RT^2\Delta Z^{lv}} \qquad \text{(Eq. 6.87)}$$

$$dT = -T^2 d(1/T)$$

$$\frac{d\ln P^{sat}}{d(1/T)} = -\frac{\Delta H^{lv}}{R\Delta Z^{lv}} \qquad \text{(Eq. 6.88)}$$

T-Dependence of Vapor Pressure

(Clausius-Clapeyron)

$$\Delta H^{lv} = -R \frac{d\ln P^{sat}}{d(1/T)}$$

➡️

$$\frac{d\ln P^{sat}}{d(1/T)} = -\frac{\Delta H^{lv}}{R} = -B$$

(constant)

$$d\ln P^{sat} = -B \cdot d(1/T)$$

➡️ Integrate:

(Eq. 6.89)

$$\ln P^{sat} = A - \frac{B}{T}$$

- Plot of ln P^{sat} vs 1/T is straight line
- A and B are constants determined from regression.
- Valid from triple point to critical point

Louis Charles Antoine, 1825-1897
"Vapor Pressure: a new relationship between pressure and temperature, *Comptes Rendus de l'Academie des Sciences* (Proceedings of the French Academy of Science), 1888, and in *Annales de Physique et de Chimie,* 1891

(Eq. 6.90)

$$\ln P^{sat} = A - \frac{B}{T+C}$$

- **Antoine Equation**
- Improved version.
- Addition of constant "C"
- Constants in Table B.2

Total Properties from Δ's

Two-Phase Liquid/Vapor Systems

For any extensive property, such as total volume nV:

$$nV = n^{liquid}V^{liquid} + n^{vapor}V^{vapor} = n^l V^l + n^v V^v$$

n = total moles
  n^l = moles of liquid
  n^v = moles of vapor

V = molar volume
  V^l = molar volume of liquid
  V^v = molar volume of vapor

$$n = n^l + n^v$$

$$\frac{n}{n} = \frac{n^l}{n} + \frac{n^v}{n}$$

$$\frac{nV}{n} = \frac{n^l V^l}{n} + \frac{n^v V^v}{n}$$

$$1 = x^l + x^v$$

$$V = x^l V^l + x^v V^v$$

$$x^v \equiv \text{quality of vapor}$$

$$V = \left(1 - x^v\right)V^l + x^v V^v$$

$$M \equiv V, U, H, S, G$$

$$M = \left(1 - x^v\right)M^l + x^v M^v \qquad \text{(Eq. 6.96a)}$$

$$M = M^l + x^v \Delta M^{lv} \qquad \text{(Eq. 6.96b)}$$

(Important for upcoming lessons)

Questions?

Homework

Problem 6.28

What is the mole fraction of water vapor in air that is saturated with water at

(a) 25°C and 101.33 kPa?

(b) 50°C and 101.33 kPa?

Problem 6.14

Estimate the entropy changes of vaporizations of benzene at 50°C. The vapor pressure of benzene is given by the equation

$$\ln\left(P^{sat}/kPa\right)=13.8858-\frac{2788.51}{\left(t/degC\right)+220.79}$$

(a) Use Eq. 6.86 with an estimated value of ΔV^{lv}.

(b) Use the Clausius-Clapeyron equation from Example 6.6.

Report your answers in J/(mol-K).

Problem 6.83

(mixtures)

An equimolar mixture of methane and propane is discharged from a compressor at 5,500 kPa and 90°C at a rate of 1.4 kg/sec. If the velocity in the discharge line is not to exceed 30 m/sec, what is the minimum diameter of the discharge line?

Use pseudocritical parameters from equations 6.78-6.82 along with the SRK equation. (Don't use the API method.)

Problem 6.25

Steam at 2,100 kPa and 260°C expands at constant enthalpy (as in a throttling process) to 125 kPa. What is the temperature of the steam in its final state and what is its entropy change?
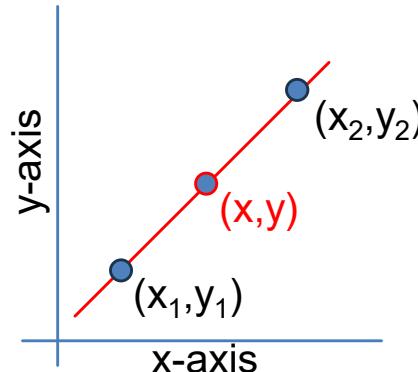
What would be the final temperature and entropy change for an ideal gas?

Study example 6.9 closely first

Problem 6.25

Steam at 2,100 kPa and 260°C expands at constant enthalpy (as in a throttling process) to 125 kPa. What is the temperature of the steam in its final state and what is its entropy change? What would be the final temperature and entropy change for an ideal gas?

Interpolation of points in steam tables

(x,y) is between (x_1,y_1) and (x_2,y_2)

y-axis

(x_2,y_2)

(x,y)

(x_1,y_1)

x-axis

$$\frac{y - y_1}{x - x_1} = \frac{y_2 - y_1}{x_2 - x_1}$$

(x_1,y_1) and (x_2,y_2) are known

rearranged:

$$\frac{x - x_1}{x_2 - x_1} = \frac{y - y_1}{y_2 - y_1}$$

either x or y is known, and the other is calculated

Remember slope is constant between two points

Finding S_1 and H_1

TABLE E.2 Properties of Superheated Steam (Continued)

TEMPERATURE: t°C
(TEMPERATURE: T kelvins)

APPENDIX E. Steam Tables

P/kPa (t^{sat}/°C)		sat. liq.	sat. vap.	200 (473.15)	225 (498.15)	250 (523.15)	275 (548.15)	300 (573.15)	325 (598.15)	350 (623.15)	375 (648.15)
1750 (205.72)	V	1.166	113.38	......	120.39	128.85	136.82	144.45	151.87	159.12	166.27
	U	876.234	2595.7	......	2637.6	2687.7	2734.5	2779.3	2822.7	2865.3	2907.4
	H	878.274	2794.1	......	2848.2	2913.2	2974.0	3032.1	3088.4	3143.7	3198.4
	S	2.3846	6.3853	......	6.4961	6.6233	6.7368	6.8405	6.9368	7.0273	7.1133
1800 (207.11)	V	1.168	110.32	......	116.69	124.99	132.78	140.24	147.48	154.55	161.51
	U	882.472	2596.3	......	2635.5	2686.1	2733.3	2778.2	2821.8	2864.5	2906.7
	H	884.574	2794.8	......	2845.5	2911.0	2972.3				
	S				6.4787	6.6071	6.7214				
1850					113.19	121.33	128.96				
					2633.3	2684.4	2732.0				
					2842.8	2908.9	2970.6				
					6.4616	6.5912	6.7064				
1900 (209.80)	V				...09.87	117.87	125.35				
	U				...31.2	2682.8	2730.7				
	H	896.807	2796.1	......	2840.0	2906.7	2968.8	3027.9	3084.9	3140.7	3195.7
	S	2.4228	6.3554	......	6.4448	6.5757	6.6917	6.7970	6.8944	6.9857	7.0723
1950 (211.10)	V	1.174	102.031	......	106.72	114.58	121.91	128.90	135.66	142.25	148.72
	U	900.461	2597.7	......	2629.0	2681.1	2729.4	2775.1	2819.2	2862.3	2904.8
	H	902.752	2796.7	......	2837.1	2904.6	2967.1	3026.5	3083.7	3139.7	3194.8
	S	2.4349	6.3459	......	6.4283	6.5604	6.6772	6.7831	6.8809	6.9725	7.0593
2000 (212.37)	V	1.177	99.536	......	103.72	111.45	118.65	125.50	132.11	138.56	144.89
	U	906.236	2598.2	......	2626.9	2679.5	2728.1	2774.0	2818.3	2861.5	2904.1
	H	908.589	2797.2	......	2834.3	2902.4	2965.4	3025.0	3082.5	3138.6	3193.9
	S	2.4469	6.3366	......	6.4120	6.5454	6.6631	6.7696	6.8677	6.9596	7.0466
2100 (214.85)	V	1.181	94.890	......	98.147	105.64	112.59	119.18	125.53	131.70	137.76
	U	917.479	2598.9	......	2622.4	2676.1	2725.4	2771.9	2816.5	2860.0	2902.8
	H	919.959	2798.2	......	2828.5	2897.9	2961.9	3022.2	3080.1	3136.6	3192.1
	S	2.4700	6.3187	......	6.3802	6.5162	6.6356	6.7432	6.8422	6.9347	7.0220
2200 (217.24)	V	1.185	90.652	......	93.067	100.35	107.07	113.43	119.53	125.47	131.28
	U	928.346	2599.6	......	2617.9	2672.7	2722.7	2769.7	2814.7	2858.5	2901.5
	H	930.953	2799.1	......	2822.7	2893.4	2958.3	3019.3	3077.7	3134.5	3190.3
	S	2.4922	6.3015	......	6.3492	6.4879	6.6091	6.7179	6.8177	6.9107	6.9985
2300 (219.55)	V	1.189	86.769	......	88.420	95.513	102.03	108.18	114.06	119.77	125.36
	U	938.866	2600.2	......	2613.3	2669.2	2720.0	2767.6	2812.9	2857.0	2900.2
	H	941.601	2799.8	......	2816.7	2888.9	2954.7	3016.4	3075.3	3132.4	3188.5
	S	2.5136	6.2849	......	6.3190	6.4605	6.5835	6.6935	6.7941	6.8877	6.9759

In[3]:= eq1 = $\dfrac{260 - 250}{275 - 250}$ == $\dfrac{s1 - 6.5162}{6.6356 - 6.5162}$;

In[4]:= Solve[eq1, s1]

Out[4]= {{s1 → 6.56396}}

$$S_1 = 6.5640 \ \frac{kJ}{kg \cdot K}$$

In[5]:= eq2 = $\dfrac{260 - 250}{275 - 250}$ == $\dfrac{h1 - 2897.9}{2961.9 - 2897.9}$;

In[6]:= Solve[eq2, h1]

Out[6]= {{h1 → 2923.5}}

$$H_1 = 2923.5 \ \frac{kJ}{kg}$$

Problem 6.25

Steam at 2,100 kPa and 260°C expands at constant enthalpy (as in a throttling process) to 125 kPa. What is the temperature of the steam in its final state and what is its entropy change? What would be the final temperature and entropy change for an ideal gas?

- T_1 = 260 degC
- P_1 = 2,100 kPa

- Superheated steam, Table E.2, page 717.
- Interpolate between 250 and 275 degC.

- S_1 = 6.5640 kJ/(kg·K)
- H_1 = 2,923.5 kJ/kg

- $H_2 = H_1$ = 2,923.5 kJ/kg
- P_2 = 125 kPa

Finding T_2 and S_2

TABLE E.2 Properties of Superheated Steam

TEMPERATURE: t°C
(TEMPERATURE: T kelvins)

P/kPa (t^{sat}/°C)		sat. liq.	sat. vap.	75 (348.15)	100 (373.15)	125 (398.15)	150 (423.15)	175 (448.15)	200 (473.15)	225 (498.15)	250 (523.15)
101.325 (100.00)	V	1.044	1673.0	......	1673.0	1792.7	1910.7	2027.7	2143.8	2259.3	2374.5
	U	418.959	2506.5	......	2506.5	2544.7	2582.6	2620.4	2658.1	2695.9	2733.9
	H	419.064	2676.0	......	2676.0	2726.4	2776.2	2825.8	2875.3	2924.8	2974.5
	S	1.3069	7.3554	......	7.3554	7.4860	7.6075	7.7213	7.8288	7.9308	8.0280
125 (105.99)	V	1.049	1374.6	......	......	1449.1	1545.6	1641.0	1735.6	1829.6	1923.2
	U	444.224	2513.4	......	......	2542.9	2581.2	2619.3	2657.2	2695.2	2733.3
	H	444.356	2685.2	......	......	2724.0	2774.4	2824.4	2874.2	2923.9	2973.7
	S	1.3740	7.2847	......	......	7.3844	7.5072	7.6219	7.7300	7.8324	7.9300
150 (111.37)	V	1.053	1159.0	......	......	1204.0	1285.2	1365.2	1444.4	1523.0	1601.3
	U	466.968	2519.5			2540.9	2579.7	2618.1	2656.3	2694.4	2732.7
	H	467.126	2693.4			2721.5	2772.5	282			
	S					7.2953	7.4194				
						1028.8	1099.1	116			
						2538.9	2578.2	261			
						2719.0	2770.5	282			
						7.2191	7.3447				
(120.23)						897.47	959.54	102			
						2536.9	2576.6	261			
	H	304.701	2706.3	......	......	2716.4	2768.5	2819.8	2870.5	2920.9	2971.2
	S	1.5301	7.1268	......	......	7.1523	7.2794	7.3971	7.5072	7.6110	7.7096
225 (123.99)	V	1.064	792.97	......	......	795.25	850.97	905.44	959.06	1012.1	1064.7
	U	520.465	2533.2	......	......	2534.8	2575.1	2614.5	2653.5	2692.2	2730.8
	H	520.705	2711.6	......	......	2713.8	2766.5	2818.2	2869.3	2919.9	2970.4
	S	1.5705	7.0873	......	......	7.0928	7.2213	7.3400	7.4508	7.5551	7.6540
250 (127.43)	V	1.068	718.44	......	......	......	764.09	813.47	861.98	909.91	957.41
	U	535.077	2536.8	......	......	......	2573.5	2613.3	2652.5	2691.4	2730.2
	H	535.343	2716.4	......	......	......	2764.5	2816.7	2868.0	2918.9	2969.6
	S	1.6071	7.0520	......	......	......	7.1689	7.2886	7.4001	7.5050	7.6042
275 (130.60)	V	1.071	657.04	......	......	......	693.00	738.21	782.55	826.29	869.61
	U	548.564	2540.0	......	......	......	2571.9	2612.1	2651.6	2690.7	2729.6
	H	548.858	2720.7	......	......	......	2762.5	2815.1	2866.8	2917.9	2968.7
	S	1.6407	7.0201	......	......	......	7.1211	7.2419	7.3541	7.4594	7.5590
300 (133.54)	V	1.073	605.56	......	......	......	633.74	675.49	716.35	756.60	796.44
	U	561.107	2543.0	......	......	......	2570.3	2610.8	2650.6	2689.9	2729.0
	H	561.429	2724.7	......	......	......	2760.4	2813.5	2865.5	2916.9	2967.9
	S	1.6716	6.9909	......	......	......	7.0771	7.1990	7.3119	7.4177	7.5176

In[9]:= eq3 = $\dfrac{t2 - 200}{225 - 200} == \dfrac{2923.5 - 2874.2}{2923.9 - 2874.2}$;

In[10]:= Solve[eq3, t2]

Out[10]= {{t2 → 224.798793}}

$T_2 = 224.80\ ^\circ C$

In[11]:= eq4 = $\dfrac{224.80 - 200}{225 - 200} == \dfrac{s2 - 7.7300}{7.8324 - 7.7300}$;

In[12]:= Solve[eq4, s2]

Out[12]= {{s2 → 7.8315808}}

$S_2 = 7.8316\ \dfrac{kJ}{kg \cdot K}$

Problem 6.25

Steam at 2,100 kPa and 260°C expands at constant enthalpy (as in a throttling process) to 125 kPa. What is the temperature of the steam in its final state and what is its entropy change? What would be the final temperature and entropy change for an ideal gas?

- T_1 = 260°C
- P_1 = 2,100 kPa

- Superheated steam, Table E.2, page 705.
- Interpolate between 250 and 275°C.

- S_1 = 6.5640 kJ/(kg·K)
- H_1 = 2,923.5 kJ/kg

- H_2 = H_1 = 2,923.5 kJ/kg
- P_2 = 125 kPa

- at 125 kPa and 200°C, H = 2,874.2 kJ/kg
- at 125 kPa and 225°C, H = 2,923.9 kJ/kg

- T_2 = 224.8°C

Problem 6.25

Steam at 2,100 kPa and 260°C expands at constant enthalpy (as in a throttling process) to 125 kPa. What is the temperature of the steam in its final state and what is its entropy change? What would be the final temperature and entropy change for an ideal gas?

- T_1 = 260 degC
- P_1 = 2,100 kPa

- Superheated steam, Table E.2, page 705.
- Interpolate between 250 and 275°C.

- S_1 = 6.5640 kJ/(kg·K)
- P_2 = 125 kPa

- at 125 kPa and 200°C, S = 7.7300 kJ/(kg·K)
- at 125 kPa and 225°C, S = 7.8324 kJ/(kg·K)

- S_2 = 7.8316 kJ/(kg·K)

- ΔS = 7.8316 – 6.5640 = 1.2676 kJ/(kg·K)

Problem 6.25

Steam at 2,100 kPa and 260°C expands at constant enthalpy (as in a throttling process) to 125 kPa. What is the temperature of the steam in its final state and what is its entropy change? What would be the final temperature and entropy change for an ideal gas?

Ideal gas:

- T_1 = 260°C
- P_1 = 2,100 kPa
- H_1 = 2,923.5 kJ/kg

- T_2 = ???
- P_2 = 125 kPa
- H_2 = 2,923.5 kJ/kg

$$\Delta H^{ig} = R \int_{T_1}^{T_2} \frac{Cp}{R} \, dT$$

$$\Delta S^{ig} = R \int_{T_1}^{T_2} \frac{Cp/R}{T} \, dT - R \, Ln\left(\frac{P_2}{P_1}\right)$$

Equation 5.10

Supplemental Slides

Example 6.9

Superheated steam originally at P_1 and T_1 expands through a nozzle to an exhaust pressure P_2. Assuming the process is reversible and adiabatic, determine the downstream state of the steam and ΔH for the following conditions:

P_1 = 1,000 kPa, T_1 = 250°C, P_2 = 200 kPa

Example 6.9

Superheated steam originally at P_1 and T_1 expands through a nozzle to an exhaust pressure P_2. Assuming the process is reversible and adiabatic, determine the downstream state of the steam and ΔH for the following conditions:

P_1 = 1,000 kPa, T_1 = 250°C, P_2 = 200 kPa

Superheated Water Tables

T Temp. °C	v m³/kg	u kJ/kg	h kJ/kg	s kJ/(kg·K)	v m³/kg	u kJ/kg	h kJ/kg	s kJ/(kg·K)
			p = 0.01 MPa (45.81°C)				p = 0.05 MPa (81.33°C)	
			p = 0.80 MPa (170.43°C)				p = 1.00 MPa (179.91°C)	
Sat.	0.2404	2576.8	2769.1	6.6628	0.194 44	2583.6	2778.1	6.5865
200	0.2608	2630.6	2839.3	6.8158	0.2060	2621.9	2827.9	6.6940
250	0.2931	2715.5	2950.0	7.0384	0.2327	2709.9	2942.6	6.9247
300	0.3241	2797.2	3056.5	7.2328	0.2579	2793.2	3051.2	7.1229
350	0.3544	2878.2	3161.7	7.4089	0.2825	2875.2	3157.7	7.3011
400	0.3843	2959.7	3267.1	7.5716	0.3066	2957.3	3263.9	7.4651
500	0.4433	3126.0	3480.6	7.8673	0.3541	3124.4	3478.5	7.7622
600	0.5018	3297.9	3699.4	8.1333	0.4011	3296.8	3697.9	8.0290
700	0.5601	3476.2	3924.2	8.3770	0.4478	3475.3	3923.1	8.2731
800	0.6181	3661.1	4155.6	8.6033	0.4943	3660.4	4154.7	8.4996
900	0.6761	3852.8	4393.7	8.8153	0.5407	3852.2	4392.9	8.7118
1000	0.7340	4051.0	4638.2	9.0153	0.5871	4050.5	4637.6	8.9119
1100	0.7919	4255.6	4889.1	9.2050	0.6335	4255.1	4888.6	9.1017
1200	0.8497	4466.1	5145.9	9.3855	0.6798	4465.6	5145.4	9.2822
1300	0.9076	4681.8	5407.9	9.5575	0.7261	4681.3	5407.4	9.4543

91 THERMODYNAMICS

H_1=2,942.6 kJ/kg

S_1=6.9247 kJ/(kg·K) =S_2

Steam tables from FE Reference Manual

At P_2 = 200 kPa

H_1=2,942.6 kJ/kg

S_1=6.9247 kJ/(kg·K) S_2=6.9247 kJ/(kg·K)

T Temp. °C	v m³/kg	u kJ/kg	h kJ/kg	s kJ/(kg·K)	v m³/kg	u kJ/kg	h kJ/kg	s kJ/(kg·K)
Superheated Water Tables								
	p = 0.01 MPa (45.81°C)				*p* = 0.05 MPa (81.33°C)			
1300	72.602	4683.7	5409.7	11.5811	14.521	4683.6	5409.6	10.8382
	p = 0.10 MPa (99.63°C)				*p* = 0.20 MPa (120.23°C)			
Sat.	1.6940	2506.1	2675.5	7.3594	0.8857	2529.5	2706.7	7.1272
100	1.6958	2506.7	2676.2	7.3614				
150	1.9364	2582.8	2776.4	7.6134	0.9596	2576.9	2768.8	7.2795
200	2.172	2658.1	2875.3	7.8343	1.0803	2654.4	2870.5	7.5066
250	2.406	2733.7	2974.3	8.0333	1.1988	2731.2	2971.0	7.7086
300	2.639	2810.4	3074.3	8.2158	1.3162	2808.6	3071.8	7.8926
400	3.103	2967.9	3278.2	8.5435	1.5493	2966.7	3276.6	8.2218
500	3.565	3131.6	3488.1	8.8342	1.7814	3130.8	3487.1	8.5133
600	4.028	3301.9	3704.4	9.0976	2.013	3301.4	3704.0	8.7770
700	4.490	3479.2	3928.2	9.3398	2.244	3478.8	3927.6	9.0194
800	4.952	3663.5	4158.6	9.5652	2.475	3663.1	4158.2	9.2449
900	5.414	3854.8	4396.1	9.7767	2.705	3854.5	4395.8	9.4566
1000	5.875	4052.8	4640.3	9.9764	2.937	4052.5	4640.0	9.6563
1100	6.337	4257.3	4891.0	10.1659	3.168	4257.0	4890.7	9.8458
1200	6.799	4467.7	5147.6	10.3463	3.399	4467.5	5147.5	10.0262
1300	7.260	4683.5	5409.5	10.5183	3.630	4683.2	5409.3	10.1982
	p = 0.40 MPa (143.63°C)				*p* = 0.60 MPa (158.85°C)			
Sat.	0.4625	2553.6	2738.6	6.8959	0.3157	2567.4	2756.8	6.7600
150	0.4708	2564.5	2752.8	6.9299				

Entropy cannot be 6.9247 kJ/(kg·K) at 200 kPa unless some of the steam condensed.

Temperature is 120.23°C if some of the steam condensed.

$H_1 = 2{,}942.6$ kJ/kg

$S_1 = 6.9247$ kJ/(kg·K) $S_1 = S_2 = 6.9247$ kJ/(kg·K)

$$S_2 = \left(1 - x^v\right)S^l + x^v S^v \qquad \text{(Eq. 6.82a)}$$

STEAM TABLES Saturated Water - Temperature Table													
Temp. °C T	Sat. Press. kPa p_{sat}	Specific Volume m³/kg		Internal Energy kJ/kg			Enthalpy kJ/kg			Entropy kJ/(kg·K)		
		Sat. liquid v_f	Sat. vapor v_g	Sat. liquid u_f	Evap. u_{fg}	Sat. vapor u_g	Sat. liquid h_f	Evap. h_{fg}	Sat. vapor h_g	Sat. liquid s_f	Evap. s_{fg}	Sat. vapor s_g
0.01	0.6113	0.001 000	206.14	0.00	2375.3	2375.3	0.01	2501.3	2501.4	0.0000	9.1562	9.1562
	MPa											
115	0.169 06	0.001 056	1.0366	482.30	2041.4	2523.7	482.48	2216.5	2699.0	1.4734	5.7100	7.1833
120	0.198 53	0.001 060	0.8919	503.50	2025.8	2529.3	503.71	2202.6	2706.3	1.5276	5.6020	7.1296
125	0.2321	0.001 065	0.7706	524.74	2009.9	2534.6	524.99	2188.5	2713.5	1.5813	5.4962	7.0775

90 THERMODYNAMICS

Pressure must be 0.200 MPa so we have to do some interpolating.

$H_1 = 2{,}942.6$ kJ/kg

$S_1 = 6.9247$ kJ/(kg·K) $S_1 = S_2 = 6.9247$ kJ/(kg·K)

$$S_2 = \left(1 - x^v\right)S^l + x^v S^v \qquad \text{(Eq. 6.82a)}$$

STEAM TABLES
Saturated Water - Temperature Table

Temp. °C T	Sat. Press. kPa p_{sat}	Specific Volume m³/kg		Internal Energy kJ/kg			Enthalpy kJ/kg			Entropy kJ/(kg·K)		
		Sat. liquid v_f	Sat. vapor v_g	Sat. liquid u_f	Evap. u_{fg}	Sat. vapor u_g	Sat. liquid h_f	Evap. h_{fg}	Sat. vapor h_g	Sat. liquid s_f	Evap. s_{fg}	Sat. vapor s_g
0.01	0.6113	0.001 000	206.14	0.00	2375.3	2375.3	0.01	2501.3	2501.4	0.0000	9.1562	9.1562
	MPa											
115	0.169 06	0.001 056	1.0366	482.30	2041.4	2523.7	482.48	2216.5	2699.0	1.4734	5.7100	7.1833
120	0.198 53	0.001 060	0.8919	503.50	2025.8	2529.3	503.71	2202.6	2706.3	1.5276	5.6020	7.1296
120.23	0.2001	←	interpolate			→				1.5301		7.1272
125	0.2321	0.001 065	0.7706	524.74	2009.9	2534.6	524.99	2188.5	2713.5	1.5813	5.4962	7.0775

90 THERMODYNAMICS

$$6.9247 = \left(1 - x^v\right)1.5301 + x^v \cdot 7.1272$$

$$x^v = 0.9638$$

$$x^l = \left(1 - x^v\right) = 0.0362$$

$H_1 = 2{,}942.6$ kJ/kg

$S_1 = 6.9247$ kJ/(kg·K) $S_1 = S_2 = 6.9247$ kJ/(kg·K)

$$S_2 = \left(1 - x^v\right)S^l + x^v S^v \qquad \text{(Eq. 6.82a)}$$

STEAM TABLES **Saturated Water - Temperature Table**											
Temp. °C T	Sat. Press. kPa p_{sat}	Specific Volume m³/kg		Internal Energy kJ/kg			Enthalpy kJ/kg			Entropy kJ/(kg·K)		
		Sat. liquid v_f	Sat. vapor v_g	Sat. liquid u_f	Evap. u_{fg}	Sat. vapor u_g	Sat. liquid h_f	Evap. h_{fg}	Sat. vapor h_g	Sat. liquid s_f	Evap. s_{fg}	Sat. vapor s_g
0.01	0.6113	0.001 000	206.14	0.00	2375.3	2375.3	0.01	2501.3	2501.4	0.0000	9.1562	9.1562
	MPa										
115	0.169 06	0.001 056	1.0366	482.30	2041.4	2523.7	482.48	2216.5	2699.0	1.4734	5.7100	7.1833
120	0.198 53	0.001 060	0.8919	503.50	2025.8	2529.3	503.71	2202.6	2706.3	1.5276	5.6020	7.1296
120.23	0.2001	←		interpolate		→	504.69		2706.6			
125	0.2321	0.001 065	0.7706	524.74	2009.9	2534.6	524.99	2188.5	2713.5	1.5813	5.4962	7.0775

90 THERMODYNAMICS

$x^l = 0.0362$

$x^v = 0.9638$

$$H_2 = 0.0362 \cdot 504.69 + 0.9638 \cdot 2706.6 = 2626.9 \frac{kJ}{kg}$$

$$\Delta H = H_2 - H_1 = 2{,}626.9 - 2{,}942.6 = -315.7 \frac{kJ}{kg}$$

Supplemental Slides 2

T-Dependence of Vapor Pressure

(Eq. 6.88)

$$\frac{d\ln P^{sat}}{d(1/T)} = -\frac{\Delta H^{lv}}{R\Delta Z^{lv}}$$

(Eq. 6.89)

Integrate: $\quad \ln P^{sat} = A - \dfrac{B}{T}$

- Plot of ln P^{sat} vs 1/T is straight line
- A and B are constants determined from regression.
- Valid from triple point to critical point

(Eq. 6.90) $\quad \ln P^{sat} = A - \dfrac{B}{T+C}$

- **Antoine Equation**
- Improved version.
- Addition of constant "C"
- Constants in Table B.2

PS10 - AAR

- Problems 6.1 and 6.4 – Generally good; one cadet used δ for ∂; one cadet did not make substitution for dU; one cadet did not indicate which variables were held constant in derivatives.

- Problem 6.12 – Many cadets did not finish the problem. Need expressions for H^R and S^R as well as Z and G^R.

- Problem 6.14 – Units! Also, parts (b), (c), and (d) follow from (a), which we did in class. Many cadets had (b) and (c) wrong but (a) and (d) correct.

- Make sure you understand Lesson 29, slides 7, 8, and 9. This is important for the WPR on Monday.

Vapor Pressure by Corresponding States (Lee-Kesler)

Totally different from Antoine/Clapeyron Approach

Uses Pitzer-type correlation

$$\ln P_r^{sat}(T_r) = \ln P_r^0(T_r) + \omega \cdot \ln P_r^1(T_r)$$

(Eq. 6.92)

$$\ln P_r^0 = 5.92714 - \frac{6.09648}{T_r} - 1.28862 \ln T_r + 0.169347 T_r^6$$

(Eq. 6.93)

$$\ln P_r^1 = 15.2518 - \frac{15.6875}{T_r} - 13.4721 \ln T_r + 0.43577 T_r^6$$

(Eq. 6.94)

reduced v.p. corresponding to 1 atm (1.01325 bar)

Lee and Kesler recommend finding acentric factor from 6.92

$$\omega = \frac{\ln P_{r_n}^{sat} - \ln P_r^0(T_{r_n})}{\ln P_r^1(T_{r_n})} - 13.4721 \ln T_r + 0.43577 T_r^6$$

(Eq. 6.95)

reduced normal b.p.

The initial and final thermodynamic equilibrium states of your system are as follows:

State 1: 1 kg liquid water at $0\,^\circ$C and 1 atm

State 2: 1 kg water ice at $0\,^\circ$C and 1 atm

You want to find the change in enthalpy, entropy, and Gibbs free energy between these two states.

Now, we know that, to get the change in entropy between two thermodynamic equilibrium states of a closed system, we need to identify a reversible path between these states and then calculate the integral of dq/T for that path. For the present situation, this can be accomplished by putting the system into contact with a constant temperature reservoir at a temperature only *slightly* lower than $0\,^\circ$C. As the liquid water freezes, its molecules lock into place (losing potential energy) and this results in a release of heat to the reservoir. So the temperature of the system never deviates significantly from $0\,^\circ$C. Since the process is at constant pressure, the change in enthalpy is equal to the heat transferred from the surroundings to the system:

$$\Delta H = q$$

where both q and ΔH are negative for this process. Since the process is also at constant temperature, the change in entropy, which is given by the integral of dq/T, is:

$$\Delta S = \frac{q}{T} = \frac{\Delta H}{T}$$

Thus, for this change from State 1 to State 2, ΔS is also negative. If we now use the change in enthalpy and the change in entropy to calculate the change in free energy between the two thermodynamic equilibrium states, we obtain:

$$\Delta G = \Delta H - T\Delta S = \Delta H - T\frac{\Delta H}{T} = 0$$