MME 2010
METALLURGICAL THERMODYNAMICS II

Review Problems

The binary system acetonitrile/nitromethane conforms closely to Raoult's law. Vapor pressures for the pure species are given by the following Antoine equations:

ln P_1^{sat}= 14.2724 – 2945.47/(T(C)+224) kPa

ln P_2^{sat}= 14.2043 – 2972.64/(T(C)+209) kPa

Calculate the total pressure for 0.6 weight % acetonitrile containing liquid phase in equilibrium with vapor at room temperature.

$$x_i P_i sat = y_i P$$

For the system n-pentane/n-heptane, the vapor pressures of the pure species are given by

$\ln P_1^{sat} = 13.8183 - 2477.07/(T(C)+233.21)$ kPa

$\ln P_2^{sat} = 13.8587 - 2911.32/(T(C)+216.64)$ kPa

Assuming Raoult's law to describe the vapor/liquid equilibrium states of this system, determine the fraction of the system that is liquid, x_1, and y_1 at 60 C and 1 atm, when the vapor composition of the system is equimolar

$$x_i P_i sat = y_i P$$

How much water must be added to 1000 ml of $NiSO_4$-water solution containing 96% $NiSO_4.6H_2O$ by volume in order to make a plating solution containing 64% $NiSO_4.6H_2O$ by volume?

Partial molar volume of $NiSO_4.6H_2O$ = 98.1 ml for 96% solution, 96.6 ml for 64% solution

Partial molar volume of H_2O = 14.5 ml for 96% solution, 17.1 ml for 64% solution

One mole of Pb at 25 C is added to a large amount of Pb-Si liquid alloy with X_{Pb}=0.5 at 473 K. Calculate the activity of lead at 473 K and 1000 K. Partial excess enthalpy and entropy of Pb are -1142.5 J/mole and 1.5 J/mole K respectively

Partial molar entropies of components in an A-B solution are given as S_o-RlnX where X is the mole fraction of component A or B. Determine the entropy change of mixing involving addition of 1 mole of B into A-B solution with X_B= 0.33 initial composition if the addition is made to

a) 3 moles of solution, b)large quantity of solution.

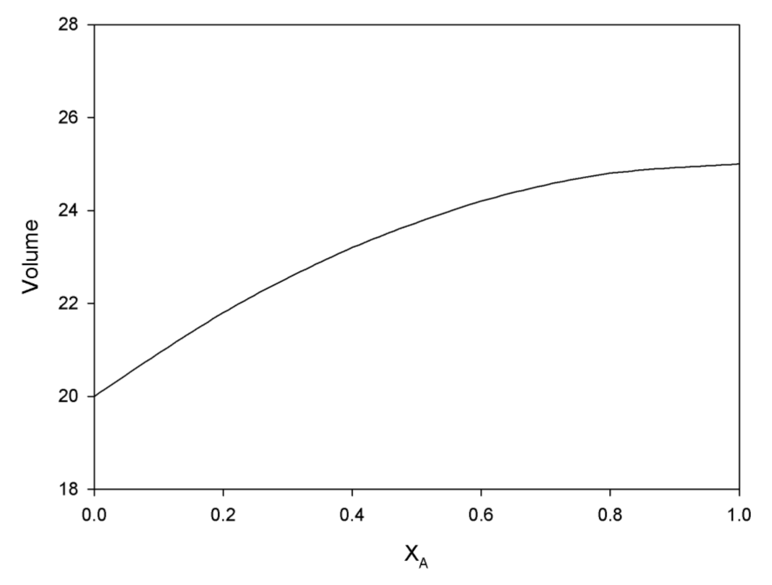
Standard entropies of A and B are 10 J/mol K and 20J/mol K respectively

Total molar enthalpy of mixing for Bi-Cd alloys at 200 C is given as 5000XbiXcd J/mole. Calculate enthalpy change of the system when 1 mole of Cd is added to a solution with X_{Bi}=0.7 if the solution is a) 2 moles, b) large quantity

Calculate the volume change of the process involving the addition of 2 moles of A into an A-B solution with x_A=0.5 initial composition when the initial solution is

a. 2 moles
b. a large quantity

The total volume of the solution is given as a function of x_A in the figure



The following equations have been proposed to represent activity coefficient data for a system at fixed T and P:

$\ln \gamma_1 = Ax_2^2 + Bx_2^2(3x_1 - x_2)$

$\ln \gamma_2 = Ax_1^2 + Bx_1^2(x_1 - 3x_2)$

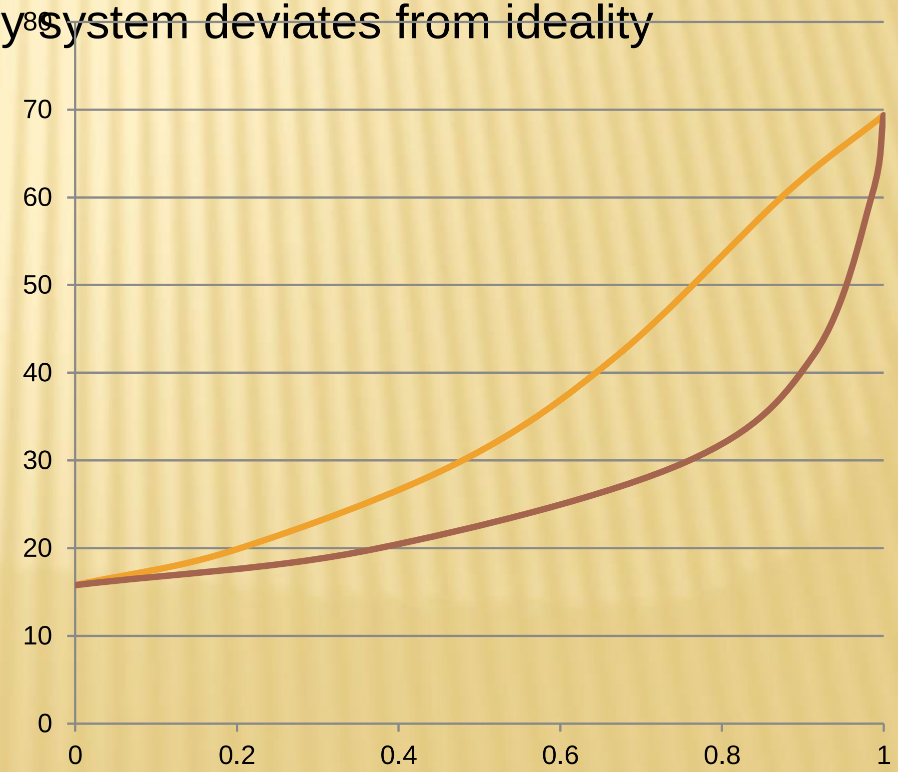
Do these equations satisfy the Gibbs/Duhem equation?

Determine an expression for G^E/RT for the system

For the binary system of chloroform/dioxane at 50 C, the following vapor-liquid equilibrium data are given:

P kPa	x_1	y_1
15.79	0.000	0.000
19.89	0.200	0.369
29.82	0.475	0.755
42.10	0.672	0.914
60.38	0.878	0.986
69.36	1.000	1.000

Determine whether the system obeys Raoult’s law or deviates from it. If there is a deviation from Raoult’s law, use modified Raoult’s law to quantify it with activity coefficient.
Explain the nature of the intermolecular interaction between chloroform and dioxane molecules for the composition range that the binary system deviates from ideality



The excess Gibbs free energy for binary systems comprised of species that are chemically similar is generally expressed as

$G^E/RT=Ax_1x_2$

Determine the value of A for a particular binary system for which the following data are avaliable for a single measurement:

T= 45 C, P= 37 kPa, x_1*= 0.398,* y_1*= 0.428*

ln P_1^{sat}*= 30.128 – 1497.07/(T(C)+592.594) kPa*

ln P_2^{sat}*= 31.425 – 1188.15/(T(C)+695.280) kPa*

Calculate $\ln\gamma_1$ *and* $\ln\gamma_2$ *values for this single data point*

$$\gamma_i x_i P_i sat = y_i P$$

$$\overline{V}_1 = V - x_1 \frac{dV}{dx_1}$$

The excess Gibbs free energy of a binary liquid mixture at a given T and P is given by

$$G^E/RT = (-1.2x_1 - 1.5x_2)\, x_1 x_2$$

Find an expression for $\ln\gamma_1$ and $\ln\gamma_2$ and show that the above equation is recovered from $G^E/RT = \sum x_i \ln\gamma_i$

Show that these equations satisty the Gibbs/Duhem equation ($\sum x_i \, d\ln\gamma_i = 0$)

$$\overline{V}_1 = V - x_1 \frac{dV}{dx_1}$$

The molar volume of a binary liquid mixture at T and P is given by

$$V = 90x_1 + 50x_2 + (6x_1 + 9x_2)x_1x_2$$

Find expressions for the partial molar volumes of species 1 and 2

Show that the above equation is recovered when these expressions are combined

Show that these expressions satisfy the Gibbs/Duhem equation

$$\overline{V}_1 = V - x_1 \frac{dV}{dx_1}$$

For a particular binary system at constant T and P, the molar enthalpies of mixtures are represented by the following equation:

$$H = x_1(a_1 + b_1 x_1) + x_2 (a_2 + b_2 x_2)$$

Determine an expression for the partial molar enthalpy of component 1.

Hint: it is not equal to $(a_1 + b_1 x_1)$

$$\overline{H}_1 = H - x_1 \frac{dH}{dx_1}$$

For a particular binary system at constant T and P, total excess enthalpy is given as
$H^E = \sum x_i A (1-x_i)$
Derive expressions for partial excess enthalpies of the components. Combine the two equations to show that the original equation is recovered

The excess volume of a binary liquid mixture of species 1 and 2 at 25 C and atmospheric pressure is given by the following equation:

$$V^E = x_1 x_2 (30x_1 + 50x_2) \text{ cm}^3/\text{mol}$$

At the same conditions V_1= 120 cm^3/mol and V_2= 150 cm^3/mol. Determine the partial molar volumes of species 1 and 2 for an equimolar mixture of species.

$$\overline{V}_1^{\,E} = V^E - x_1 \frac{dV^E}{dx_1}$$

Partial molar volume for one of the components of a binary solution at standard T and P is represented as:

$$\overline{V_A} = 3Xb^2(Xa + 3Xb)\ cm^3$$

Find an expression for the total volume of the system if the molar volume of pure B is 1 cm^3

$$\frac{V}{X_B} - {V_B}^o = \int_{X_A=0}^{X_A} \frac{\overline{V}_A dX_A}{{X_B}^2}$$

What is the heat effect per mole of solution when LiCl.3H2O(s) and H2O(l) are mixed isothermally at 25 C to form a solution containing 8 moles of water for each mole of LiCl ?

$LiCl(s)$	$-408610\ J$
$LiCl.H_2O(s)$	$-712580\ J$
$LiCl.2H_2O(s)$	$-1012650\ J$
$LiCl.3H_2O(s)$	$-1311300\ J$
$LiCl\ in\ 3\ moles\ H_2O$	$-429366\ J$
$LiCl\ in\ 5\ moles\ H_2O$	$-436805\ J$
$LiCl\ in\ 8\ moles\ H_2O$	$-440529\ J$
$LiCl\ in\ 10\ moles\ H_2O$	$-441579\ J$
$LiCl\ in\ 12\ moles\ H_2O$	$-442224\ J$
$LiCl\ in\ 15\ moles\ H_2O$	$-442835\ J$

What is the heat effect when 30 kg of LiCl(s) is added to 150 kg of an aqueous solution containing 15 wt% LiCl in an isothermal process at 25 C? MW_{LiCl}=42.39g

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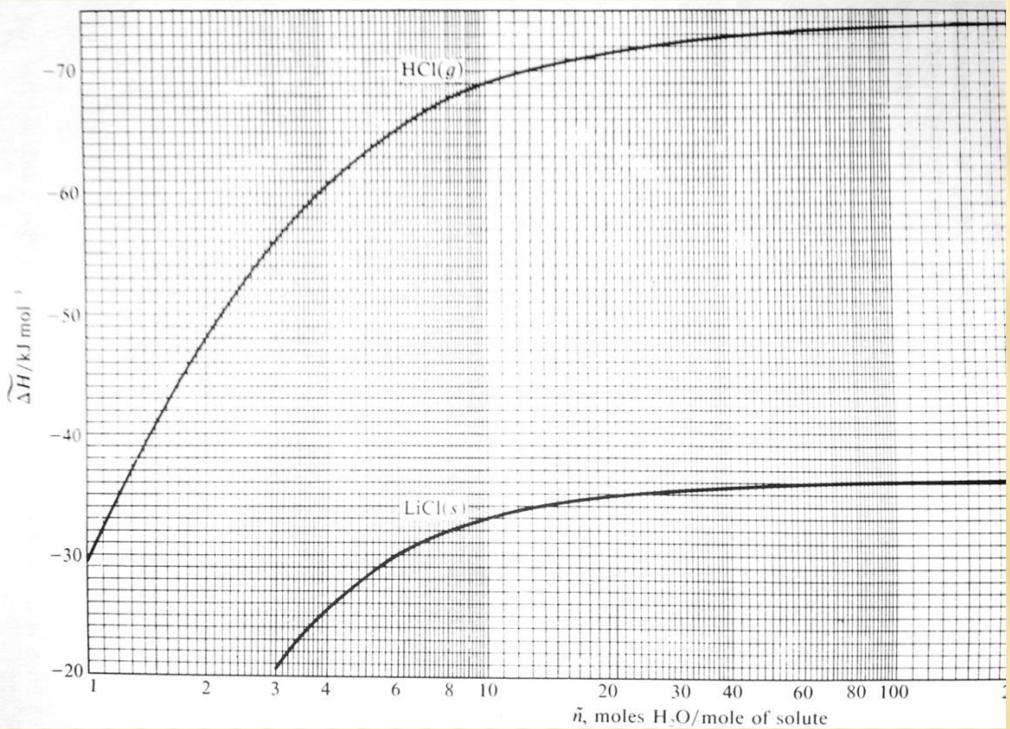
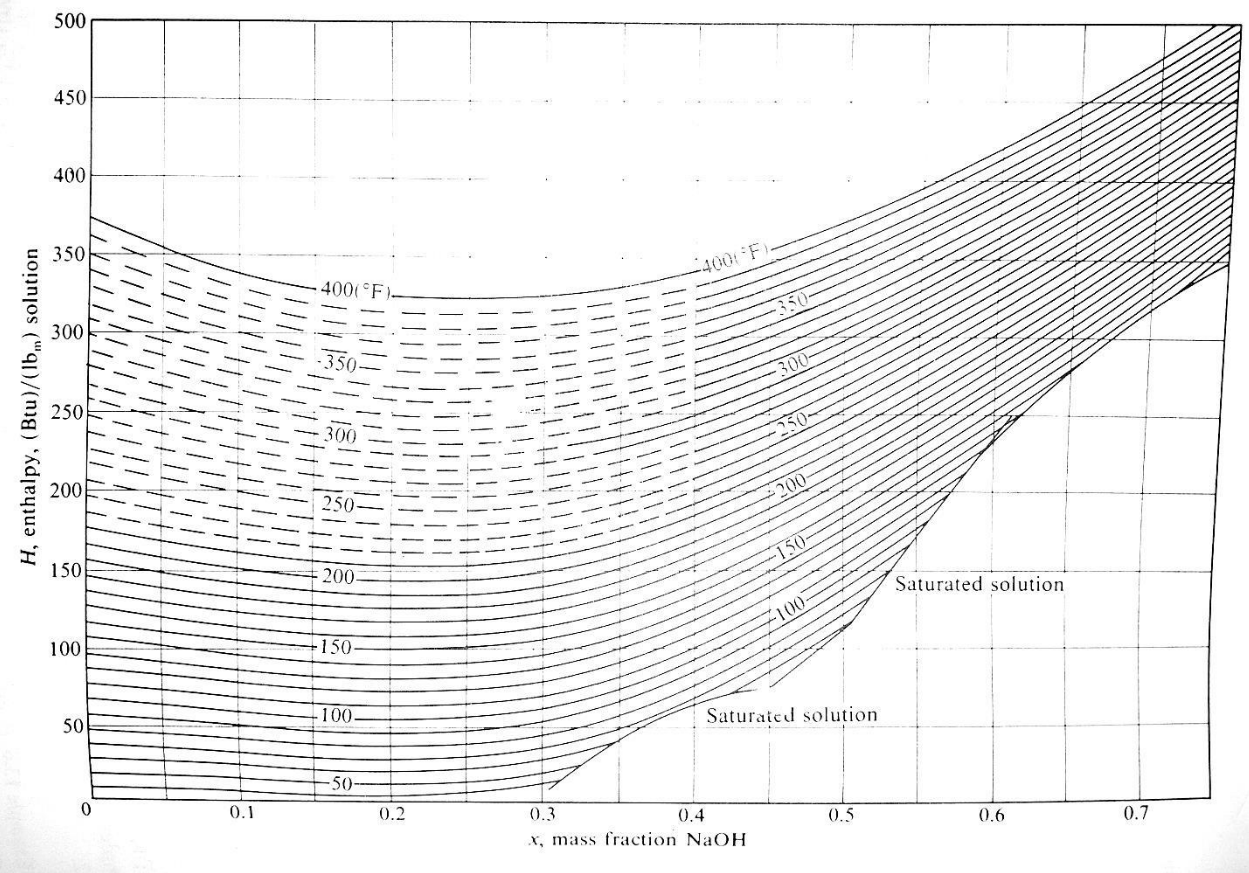
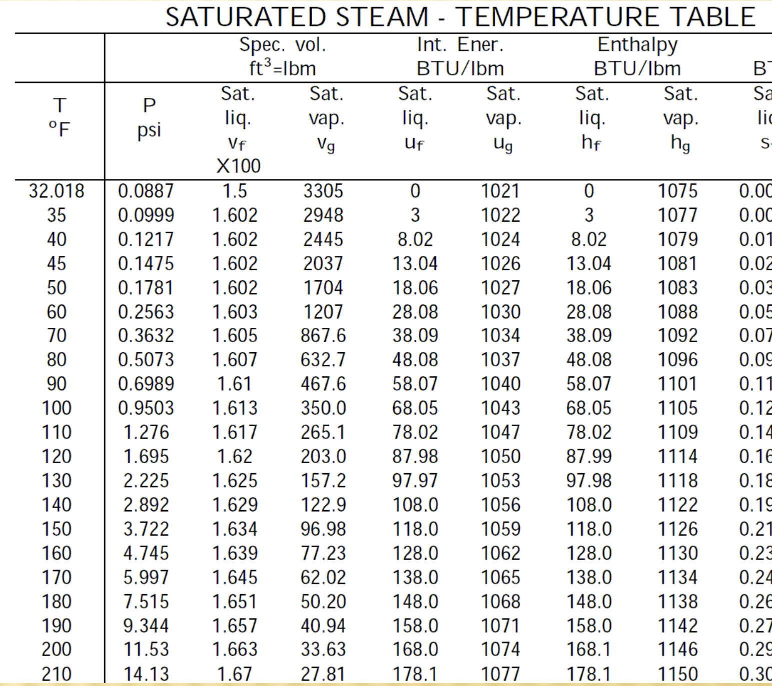
$LiCl\ in\ 12\ moles\ H_2O$	$-442224\ J$
$LiCl\ in\ 15\ moles\ H_2O$	$-442835\ J$

A liquid solution of LiCl in water at 25 C contains 1 mole of LiCl and 12 moles of water. What is the heat effect when an additional half mole of LiCl(s) is dissolved isothermally in the solution?



An evaporator concentrates 10000 lb/hr of a 10 wt% aqueous solution of NaOH to 50%. The evaporator operates at an absolute pressure of 1 atm and the boiling point of a 50% solution of NaOH is 190 F under these conditions. The feed enters at 70 F. What is the heat transfer rate in the evaporator?

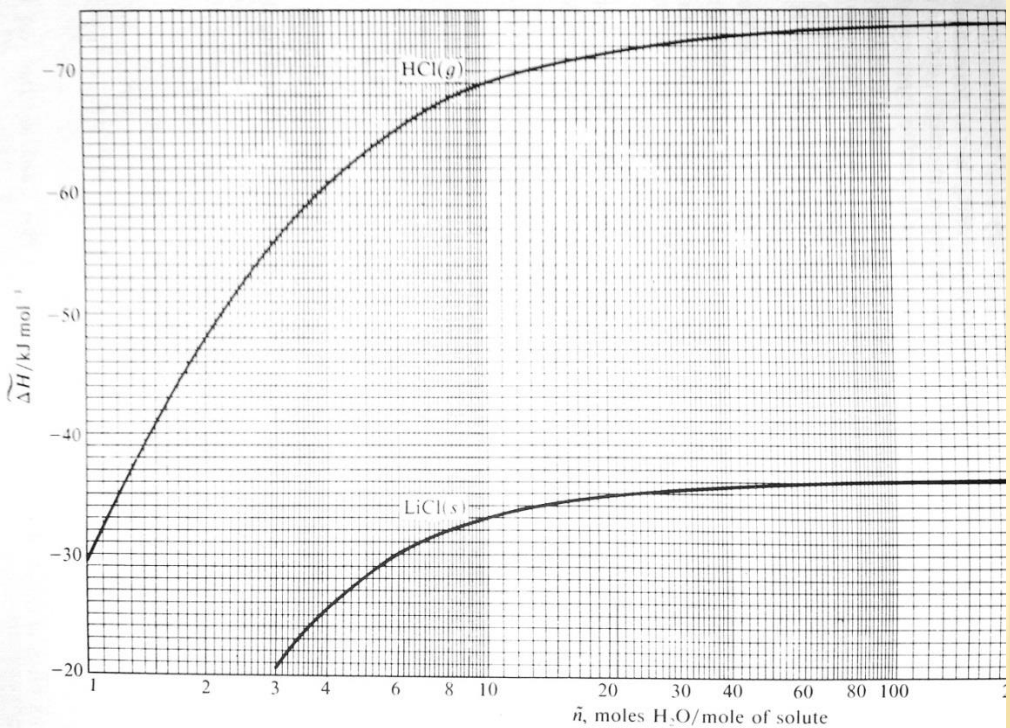


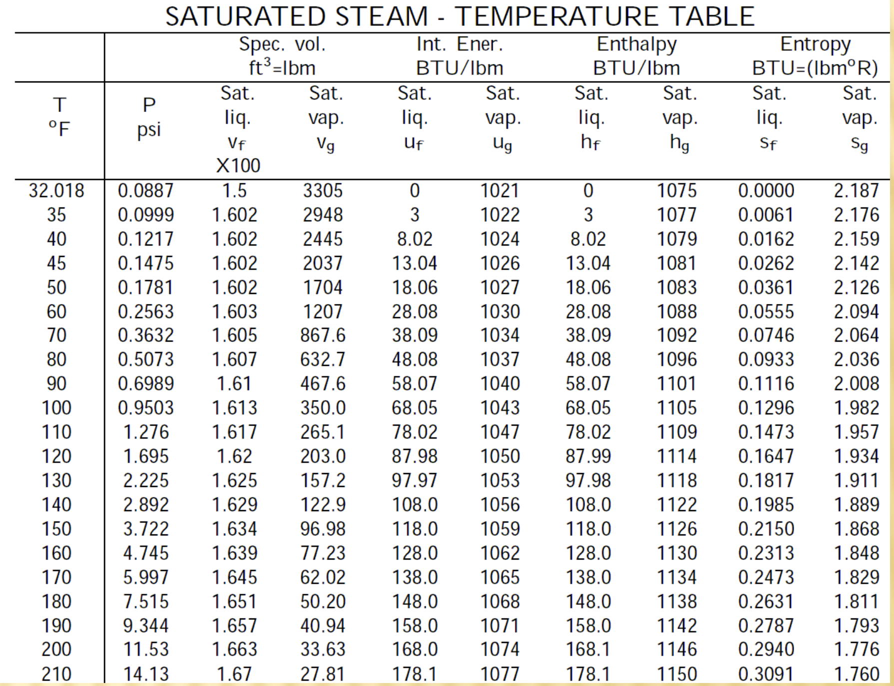


SATURATED STEAM - TEMPERATURE TABLE

		Spec. vol. ft³=lbm		Int. Ener. BTU/lbm		Enthalpy BTU/lbm		BT
T °F	P psi	Sat. liq. v_f X100	Sat. vap. v_g	Sat. liq. u_f	Sat. vap. u_g	Sat. liq. h_f	Sat. vap. h_g	Sa lic s
32.018	0.0887	1.5	3305	0	1021	0	1075	0.00
35	0.0999	1.602	2948	3	1022	3	1077	0.00
40	0.1217	1.602	2445	8.02	1024	8.02	1079	0.01
45	0.1475	1.602	2037	13.04	1026	13.04	1081	0.02
50	0.1781	1.602	1704	18.06	1027	18.06	1083	0.03
60	0.2563	1.603	1207	28.08	1030	28.08	1088	0.05
70	0.3632	1.605	867.6	38.09	1034	38.09	1092	0.07
80	0.5073	1.607	632.7	48.08	1037	48.08	1096	0.09
90	0.6989	1.61	467.6	58.07	1040	58.07	1101	0.11
100	0.9503	1.613	350.0	68.05	1043	68.05	1105	0.12
110	1.276	1.617	265.1	78.02	1047	78.02	1109	0.14
120	1.695	1.62	203.0	87.98	1050	87.99	1114	0.16
130	2.225	1.625	157.2	97.97	1053	97.98	1118	0.18
140	2.892	1.629	122.9	108.0	1056	108.0	1122	0.19
150	3.722	1.634	96.98	118.0	1059	118.0	1126	0.21
160	4.745	1.639	77.23	128.0	1062	128.0	1130	0.23
170	5.997	1.645	62.02	138.0	1065	138.0	1134	0.24
180	7.515	1.651	50.20	148.0	1068	148.0	1138	0.26
190	9.344	1.657	40.94	158.0	1071	158.0	1142	0.27
200	11.53	1.663	33.63	168.0	1074	168.1	1146	0.29
210	14.13	1.67	27.81	178.1	1077	178.1	1150	0.30

What is the concentration of the final solution when 20 moles of HCl(s) is dissolved adiabatically in 100 moles of 10% aqueous HCl solution?

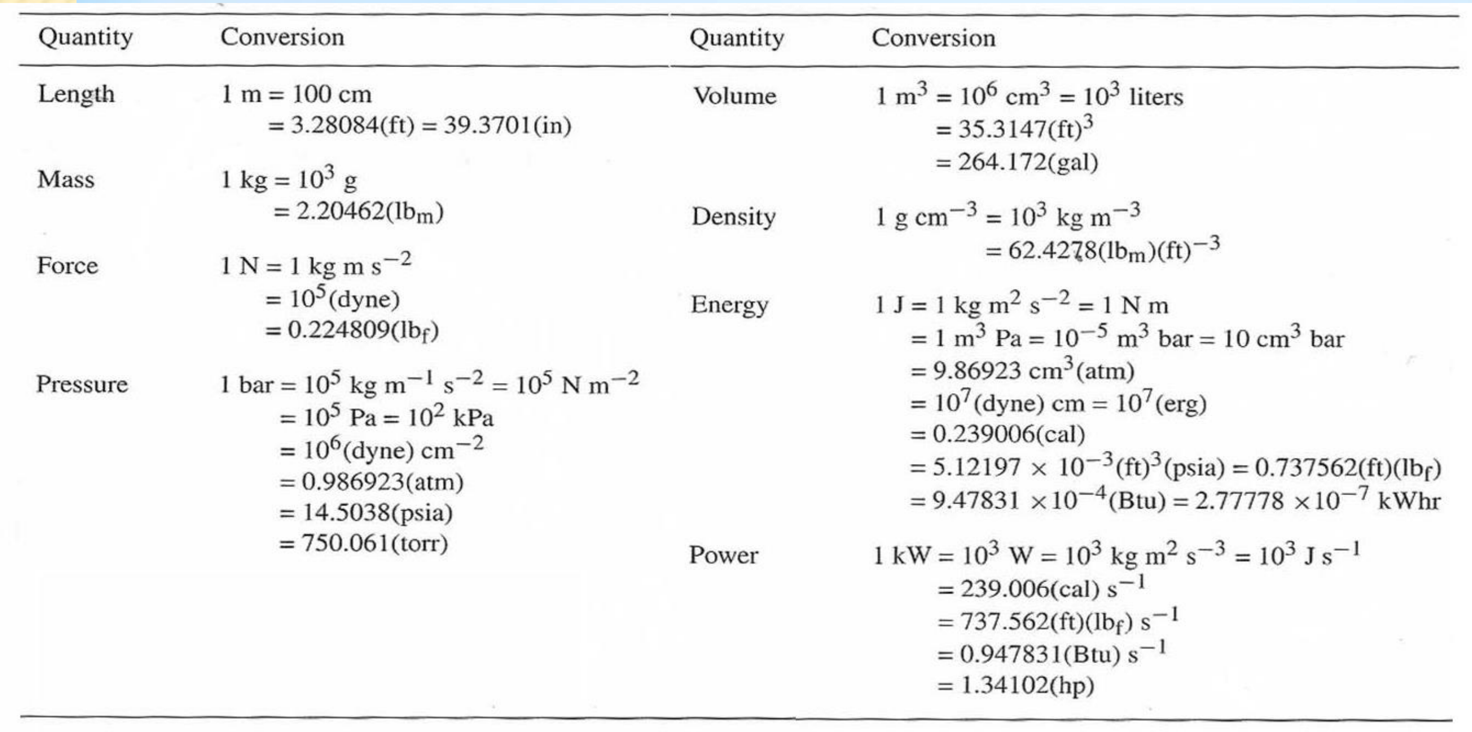




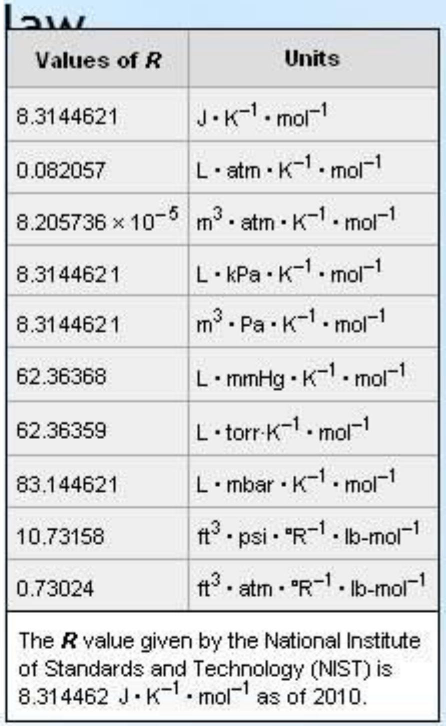
SATURATED STEAM - TEMPERATURE TABLE

T °F	P psi	Spec. vol. ft³=lbm Sat. liq. v_f X100	Sat. vap. v_g	Int. Ener. BTU/lbm Sat. liq. u_f	Sat. vap. u_g	Enthalpy BTU/lbm Sat. liq. h_f	Sat. vap. h_g	Entropy BTU=(lbm°R) Sat. liq. s_f	Sat. vap. s_g
32.018	0.0887	1.5	3305	0	1021	0	1075	0.0000	2.187
35	0.0999	1.602	2948	3	1022	3	1077	0.0061	2.176
40	0.1217	1.602	2445	8.02	1024	8.02	1079	0.0162	2.159
45	0.1475	1.602	2037	13.04	1026	13.04	1081	0.0262	2.142
50	0.1781	1.602	1704	18.06	1027	18.06	1083	0.0361	2.126
60	0.2563	1.603	1207	28.08	1030	28.08	1088	0.0555	2.094
70	0.3632	1.605	867.6	38.09	1034	38.09	1092	0.0746	2.064
80	0.5073	1.607	632.7	48.08	1037	48.08	1096	0.0933	2.036
90	0.6989	1.61	467.6	58.07	1040	58.07	1101	0.1116	2.008
100	0.9503	1.613	350.0	68.05	1043	68.05	1105	0.1296	1.982
110	1.276	1.617	265.1	78.02	1047	78.02	1109	0.1473	1.957
120	1.695	1.62	203.0	87.98	1050	87.99	1114	0.1647	1.934
130	2.225	1.625	157.2	97.97	1053	97.98	1118	0.1817	1.911
140	2.892	1.629	122.9	108.0	1056	108.0	1122	0.1985	1.889
150	3.722	1.634	96.98	118.0	1059	118.0	1126	0.2150	1.868
160	4.745	1.639	77.23	128.0	1062	128.0	1130	0.2313	1.848
170	5.997	1.645	62.02	138.0	1065	138.0	1134	0.2473	1.829
180	7.515	1.651	50.20	148.0	1068	148.0	1138	0.2631	1.811
190	9.344	1.657	40.94	158.0	1071	158.0	1142	0.2787	1.793
200	11.53	1.663	33.63	168.0	1074	168.1	1146	0.2940	1.776
210	14.13	1.67	27.81	178.1	1077	178.1	1150	0.3091	1.760

Gas constant R



Quantity	Conversion
Length	1 m = 100 cm = 3.28084(ft) = 39.3701(in)
Mass	1 kg = 10^3 g = 2.20462(lb_m)
Force	1 N = 1 kg m s^{-2} = 10^5(dyne) = 0.224809(lb_f)
Pressure	1 bar = 10^5 kg m^{-1} s^{-2} = 10^5 N m^{-2} = 10^5 Pa = 10^2 kPa = 10^6(dyne) cm^{-2} = 0.986923(atm) = 14.5038(psia) = 750.061(torr)
Volume	1 m^3 = 10^6 cm^3 = 10^3 liters = 35.3147$(ft)^3$ = 264.172(gal)
Density	1 g cm^{-3} = 10^3 kg m^{-3} = 62.4278(lb_m)$(ft)^{-3}$
Energy	1 J = 1 kg m^2 s^{-2} = 1 N m = 1 m^3 Pa = 10^{-5} m^3 bar = 10 cm^3 bar = 9.86923 cm^3(atm) = 10^7(dyne) cm = 10^7(erg) = 0.239006(cal) = 5.12197 × $10^{-3}$$(ft)^3$(psia) = 0.737562(ft)($lb_f$) = 9.47831 × 10^{-4}(Btu) = 2.77778 × 10^{-7} kWhr
Power	1 kW = 10^3 W = 10^3 kg m^2 s^{-3} = 10^3 J s^{-1} = 239.006(cal) s^{-1} = 737.562(ft)(lb_f) s^{-1} = 0.947831(Btu) s^{-1} = 1.34102(hp)



Values of *R*	**Units**
8.3144621	J · K^{-1} · mol^{-1}
0.082057	L · atm · K^{-1} · mol^{-1}
8.205736 × 10^{-5}	m^3 · atm · K^{-1} · mol^{-1}
8.3144621	L · kPa · K^{-1} · mol^{-1}
8.3144621	m^3 · Pa · K^{-1} · mol^{-1}
62.36368	L · mmHg · K^{-1} · mol^{-1}
62.36359	L · torr·K^{-1} · mol^{-1}
83.144621	L · mbar · K^{-1} · mol^{-1}
10.73158	ft^3 · psi · °R^{-1} · lb-mol^{-1}
0.73024	ft^3 · atm · °R^{-1} · lb-mol^{-1}

The ***R*** value given by the National Institute of Standards and Technology (NIST) is 8.314462 J · K^{-1} · mol^{-1} as of 2010.

Volume per gram-mole of ideal gas at 0 °C and 1 atm is 22.414 liters accordin
Avogadro's law

Thus $$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} = \frac{1\ atm * 22.414\ liters}{273.15\ degree * mole} = 0.082057\ ^{liter * atm}/_{degree * mole}$$