Lecture 1

Exercise 1: Among the following statements about thermodynamics, which one is incorrect?

(A) It can tell the feasibility of a new chemical process. can it work or not

(B) It can estimate the speed of chemical reactions. ✓

(C) It can be used to analyze the energy flow.

(D) It can be used to study the phase equilibrium.

At 27°C the reading on a manometer filled with mercury is 60.5 cm. The local acceleration of gravity is 9.784 $m \cdot s^{-2}$. To what pressure does this height of mercury correspond?

Sol: At 27°C, the density of mercury is $13.53\ g/cm^3$.

$$P = \rho g h = 13.53\ g/cm^3 \times 9.784\ m \cdot s^{-2} \times 60.5\ cm = 8.0088\ kg \cdot m \cdot s^{-2}$$

$$P\ (\text{unit } Pa) = \frac{F}{A}\ \left(\text{unit } \frac{N}{m^2}\right)$$

- m=5kg received 1000J of heat and changes its internal energy by 100 J/kg, what is the work?

Sol:

$$\Delta U = 100\ J/kg$$

$$\Delta U^t = 100\ J/kg \cdot 5\ kg = 500\ J$$

$$\Delta U^t = W + Q$$

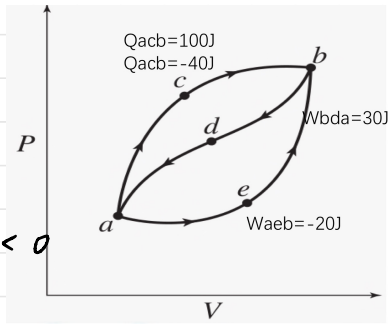
$$W = \Delta U^t - Q = 500\ J - 1000\ J = -500\ J$$

Lecture 2

When a system is taken from state *a* to state *b* in the accompanying figure along path *acb*, 100 J of heat flows into the system and the system does 40 J of work.

(*a*) How much heat flows into the system along path *aeb* if the work done by the system is 20 J?

(*b*) The system returns from *b* to *a* along path *bda*. If the work done on the system is 30 J, does the system absorb or liberate heat? How much?



Sol: (a) $\Delta U = W + Q = -40J + 100J = 60J$

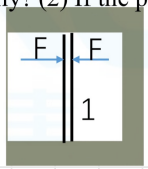
$W_{aeb} = -20J$

$Q_{aeb} = \Delta U - W_{aeb} = 60J - (-20J) = 80J$

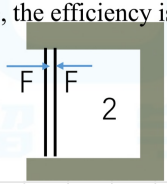
(b) $Q_{another} = \Delta U_{b\to a} - W_{another} = -60J - (30J) = -90J < 0$

liberate heat

The piston/cylinder is placed in a constant temperature bath, piston slides in the cylinder with negligible friction the gas expands against a piston isothermally. If $P = \frac{K}{V^t}$, K is a constant. (1) what is the work done by the gas reducing the external force gradually? (2) If the process is not reversible, the efficiency is 80%, what is the wo



$P_1 = 14bar$
$V_1 = 0.03\ m^3$



$P_2 = ?$
$V_2 = 0.06\ m^3$

Sol: $W_{rev} = -\int_{V_1}^{V_2} P_{ext}\, dV = -\int_{V_1}^{V_2} P_{in}\, dV$

According to $P = \frac{K}{V^t}$, $K = PV^t = 14bar \times 10^5 Pa/bar \times 0.03m^3$

$= 42000J$

$P_2 = \frac{K}{V_2^t} = \frac{42000J}{0.06m^3} = 7bar$

$W_{rev} = -\int_{V_1}^{V_2} P_2\, dV = -\int_{V_1}^{V_2} \frac{K}{V}\, dV = -K(\ln\frac{V_2}{V_1}) = -42000J \cdot \ln(\frac{0.06}{0.03})$

$= -29112J$

$W_{irreversible} = \eta W_{rev} = 0.8 \times (-29112J) = -23290J$

Lecture 3

The ideal gas undergoes:
(a) Adiabatic compression from 70 °C, 1 bar to 150 °C, P_2
(b) Isobaric cooling from 150 °C, P_2 to 70 °C, P_3
(c) Isothermal expansion from 70 °C, P_3 back to 70 °C, 1 bar

Calculate the work, heat, ΔU, ΔH for each process and in total. Given $C_V = 12.471 \frac{J}{molK}$, $C_P = 20.785 \frac{J}{molK}$

a). Sol: $\gamma = \frac{C_p}{C_V} = \frac{20.785 J \cdot mol^{-1} \cdot K^{-1}}{12.471 J \cdot mol^{-1} \cdot K^{-1}} = 1.667$

Adiabatic process (compression): $TP^{\frac{1-\gamma}{\gamma}} = Const.$

$(70+273.15)K \cdot 1bar = (150+273.15)K \cdot P_2 \Rightarrow P_2 = 0.81094\ bar$

$W = \Delta U = \int_{T_1}^{T_2} C_V^{ig} dT = C_V^{ig}(T_2 - T_1) = 12.471 J \cdot mol^{-1} \cdot K^{-1} \cdot (150+273.15-70-273.15)K = 997.68 J \cdot mol^{-1}$

$\Delta H = \int_{T_1}^{T_2} C_P^{ig} dT = C_P^{ig}(T_2 - T_1) = 20.785 J \cdot mol^{-1} \cdot K^{-1} \cdot 80K = 1662.8 J \cdot mol^{-1}$

$Q_{12} = 0$ ← adiabatic process

$\Delta U = W + Q = 997.68 J \cdot mol^{-1}$

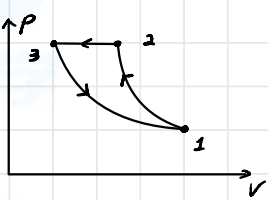
b) Sol: Isobaric process (Const. P)

$\Delta U = \int_{T_2}^{T_3} C_V^{ig} dT = C_V^{ig}(T_3 - T_2) = 12.471 J \cdot mol^{-1} \cdot K^{-1} \cdot (70+273.15-150-273.15)K = -997.68 J \cdot mol^{-1}$

$Q_{23} = \Delta H = \int_{T_2}^{T_3} C_P^{ig} dT = C_P^{ig}(T_3 - T_2) = 20.785 J \cdot mol^{-1} \cdot K^{-1} (-80K) = -1662.8 J \cdot mol^{-1}$

$W = \Delta U - Q_{23} = -997.68 J \cdot mol^{-1} - (-1662.8 J \cdot mol^{-1}) = 665.12 J \cdot mol^{-1}$

c) Sol: Isothermal process (Const. T)



$\Delta H = \Delta U = 0$

$Q_{31} = -W_{31} = \int_{V_3}^{V_1} P dV = RT_3 \ln(\frac{V_1}{V_3}) = RT \ln(\frac{P_3}{P_1})$

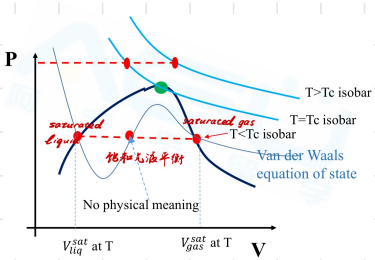
$= 8.314 J \cdot mol^{-1} \cdot K^{-1} \cdot (70+273.15)K \cdot \ln(\frac{1.689}{1}) = 1495.335 J \cdot mol^{-1}$

$W_{31} = -1495.335 J \cdot mol^{-1}$

$W_{tot} = W_{12} + W_{23} + W_{31} = 997.68 J \cdot mol^{-1} + 665.12 J \cdot mol^{-1} - 1495.335 J \cdot mol^{-1} = 167.465 J \cdot mol^{-1}$

$Q_{tot} = Q_{12} + Q_{23} + Q_{31} = 0 J \cdot mol^{-1} + (-1662.8 J \cdot mol^{-1}) + 1495.335 J \cdot mol^{-1} = -167.465 J \cdot mol^{-1}$

Example: Use Van der Waals EOS $P = \frac{RT}{V-b} - \frac{a}{V^2}$ to find V for saturated liquid and saturated vapor for n-butane at P=9.46 bar, T=350K, a= 1466.2 $\frac{L^2 kPa}{mol^2}$, b=0.1226 $\frac{L}{mol}$, R= 8.314 $\frac{J}{mol*K}$



Sol: $P = \frac{RT}{V-b} - \frac{a}{V^2}$

$\frac{RT}{V-b} = P + \frac{a}{V^2}$

$V - b = \frac{RT}{P + \frac{a}{V^2}}$

$V = \frac{RT}{P + \frac{a}{V^2}} + b$

For T=350k, $a = 1466.2 \frac{L^2 kPa}{mol^2}$

若使用迭代，无法得到中间虚根

迭代: Assume $V_{vol,1} = 0.15 L/mol$

$V_{new,1} = \frac{RT}{P + \frac{a}{V_{vol,1}^2}} + b = 0.167 L/mol$ ↳ 代入使用 P=946 kPa

$V_{new,2} = \frac{RT}{P + \frac{a}{V_{new,1}}} + b = 0.177 L/mol$

$V_{new} = 0.20 L/mol$

$V_1 = 0.20 L/mol$, saturated liquid

$V_2 = 0.36 L/mol$ (虚根)

$V_3 = 2.64 L/mol$, saturated vapor

Lecture 3

Example 3.10

Determine the molar volume of n-butane at 510K and 25bar based on each of the following:
(a) The ideal gas state, (b) the Pitzer correlation.

T_r = reduced Temp. = $\frac{T}{T_c}$ (critical temp.)

P_r = reduced Pressure = $\frac{P}{P_c}$ (critical pressure)

$PV = ZRT$ (Compressibility factor chart)

$Z = Z^0 + \omega Z^1$

Table B1 to find T_c, P_c and ω.

Table D to find Z^0 and Z^1.

$T_r = \frac{510k}{425.1k} = 1.200$ $\omega = 0.200$

$P_r = \frac{25bar}{37.96bar} = 0.659$

Table B.1: Characteristic Properties of Pure Species

	Molar mass	ω	T_c/K	P_c/bar	Z_c	V_c cm^3·mol^{-1}	T_n/K
Methane	16.043	0.012	190.6	45.99	0.286	98.6	111.4
Ethane	30.070	0.100	305.3	48.72	0.279	145.5	184.6
Propane	44.097	0.152	369.8	42.48	0.276	200.0	231.1
n-Butane	58.123	0.200	425.1	37.96	0.274	255.	272.7
n-Pentane	72.150	0.252	469.7	33.70	0.270	313.	309.2
n-Hexane	86.177	0.301	507.6	30.25	0.266	371.	341.9
n-Heptane	100.204	0.350	540.2	27.40	0.261	428.	371.6
n-Octane	114.231	0.400	568.7	24.90	0.256	486.	398.8
n-Nonane	128.258	0.444	594.6	22.90	0.252	544.	424.0
n-Decane	142.285	0.492	617.7	21.10	0.247	600.	447.3
Isobutane	58.123	0.181	408.1	36.48	0.282	262.7	261.4
Isooctane	114.231	0.302	544.0	25.68	0.266	468.	372.4

Table D.2: Values of Z^1

P_r =	0.0100	0.0500	0.1000	0.2000	0.4000	0.6000	0.8000	1.0000
T_r								
0.30	*−0.0008*	*−0.0040*	*−0.0081*	*−0.0161*	*−0.0323*	*−0.0484*	*−0.0645*	−0.0806
0.35	*−0.0009*	*−0.0046*	*−0.0093*	*−0.0185*	*−0.0370*	*−0.0554*	*−0.0738*	−0.0921
0.40	*−0.0010*	*−0.0048*	*−0.0095*	*−0.0190*	*−0.0380*	*−0.0570*	*−0.0758*	−0.0946
0.45	*−0.0009*	*−0.0047*	*−0.0094*	*−0.0187*	*−0.0374*	*−0.0560*	*−0.0745*	−0.0929
0.50	*−0.0009*	*−0.0045*	*−0.0090*	*−0.0181*	*−0.0360*	*−0.0539*	*−0.0716*	−0.0893
0.55	−0.0314	*−0.0043*	*−0.0086*	*−0.0172*	*−0.0343*	*−0.0513*	*−0.0682*	−0.0849
0.60	−0.0205	*−0.0041*	*−0.0082*	*−0.0164*	*−0.0326*	*−0.0487*	*−0.0646*	−0.0803
0.65	−0.0137	−0.0772	*−0.0078*	*−0.0156*	*−0.0309*	*−0.0461*	*−0.0611*	−0.0759
0.70	−0.0093	−0.0507	−0.1161	*−0.0148*	*−0.0294*	*−0.0438*	*−0.0579*	−0.0718
0.75	−0.0064	−0.0339	−0.0744	*−0.0143*	*−0.0282*	*−0.0417*	*−0.0550*	−0.0681
0.80	−0.0044	−0.0228	−0.0487	−0.1160	*−0.0272*	*−0.0401*	*−0.0526*	−0.0648
0.85	−0.0029	−0.0152	−0.0319	−0.0715	*−0.0268*	*−0.0391*	*−0.0509*	−0.0622
0.90	−0.0019	−0.0099	−0.0205	−0.0442	−0.1118	*−0.0396*	*−0.0503*	−0.0604
0.93	−0.0015	−0.0075	−0.0154	−0.0326	−0.0763	−0.1662	*−0.0514*	−0.0602
0.95	−0.0012	−0.0062	−0.0126	−0.0262	−0.0589	−0.1110	*−0.0540*	−0.0607
0.97	−0.0010	−0.0050	−0.0101	−0.0208	−0.0450	−0.0770	−0.1647	−0.0623
0.98	−0.0009	−0.0044	−0.0090	−0.0184	−0.0390	−0.0641	−0.1100	−0.0641
0.99	−0.0008	−0.0039	−0.0079	−0.0161	−0.0335	−0.0531	−0.0796	−0.0680
1.00	−0.0007	−0.0034	−0.0069	−0.0140	−0.0285	−0.0435	−0.0588	−0.0879
1.01	−0.0006	−0.0030	−0.0060	−0.0120	−0.0240	−0.0351	−0.0429	−0.0223
1.02	−0.0005	−0.0026	−0.0051	−0.0102	−0.0198	−0.0277	−0.0303	−0.0062
1.05	−0.0003	−0.0015	−0.0029	−0.0054	−0.0092	−0.0097	−0.0032	0.0220
1.10	0.0000	0.0000	0.0001	0.0007	0.0038	0.0106	0.0236	0.0476
1.15	0.0002	0.0011	0.0023	0.0052	0.0127	0.0237	0.0396	0.0625
1.20	0.0004	0.0019	0.0039	0.0084	0.0190	0.0326	0.0499	0.0719

Table D.1: Values of Z^0

P_r =	0.0100	0.0500	0.1000	0.2000	0.4000	0.6000	0.8000	1.0000
T_r								
0.30	*0.0029*	*0.0145*	*0.0290*	*0.0579*	*0.1158*	*0.1737*	*0.2315*	0.2892
0.35	*0.0026*	*0.0130*	*0.0261*	*0.0522*	*0.1043*	*0.1564*	*0.2084*	0.2604
0.40	*0.0024*	*0.0119*	*0.0239*	*0.0477*	*0.0953*	*0.1429*	*0.1904*	0.2379
0.45	*0.0022*	*0.0110*	*0.0221*	*0.0442*	*0.0882*	*0.1322*	*0.1762*	0.2200
0.50	*0.0021*	*0.0103*	*0.0207*	*0.0413*	*0.0825*	*0.1236*	*0.1647*	0.2056
0.55	0.9804	*0.0098*	*0.0195*	*0.0390*	*0.0778*	*0.1166*	*0.1553*	0.1939
0.60	0.9849	*0.0093*	*0.0186*	*0.0371*	*0.0741*	*0.1109*	*0.1476*	0.1842
0.65	0.9881	0.9377	*0.0178*	*0.0356*	*0.0710*	*0.1063*	*0.1415*	0.1765
0.70	0.9904	0.9504	0.8958	*0.0344*	*0.0687*	*0.1027*	*0.1366*	0.1703
0.75	0.9922	0.9598	0.9165	*0.0336*	*0.0670*	*0.1001*	*0.1330*	0.1656
0.80	0.9935	0.9669	0.9319	0.8539	*0.0661*	*0.0985*	*0.1307*	0.1626
0.85	0.9946	0.9725	0.9436	0.8810	*0.0661*	*0.0983*	*0.1301*	0.1614
0.90	0.9954	0.9768	0.9528	0.9015	0.7800	*0.1006*	*0.1321*	0.1630
0.93	0.9959	0.9790	0.9573	0.9115	0.8059	0.6635	*0.1359*	0.1664
0.95	0.9961	0.9803	0.9600	0.9174	0.8206	0.6967	*0.1410*	0.1705
0.97	0.9963	0.9815	0.9625	0.9227	0.8338	0.7240	0.5580	0.1779
0.98	0.9965	0.9821	0.9637	0.9253	0.8398	0.7360	0.5887	0.1844
0.99	0.9966	0.9826	0.9648	0.9277	0.8455	0.7471	0.6138	0.1959
1.00	0.9967	0.9832	0.9659	0.9300	0.8509	0.7574	0.6355	0.2901
1.01	0.9968	0.9837	0.9669	0.9322	0.8561	0.7671	0.6542	0.4648
1.02	0.9969	0.9842	0.9679	0.9343	0.8610	0.7761	0.6710	0.5146
1.05	0.9971	0.9855	0.9707	0.9401	0.8743	0.8002	0.7130	0.6026
1.10	0.9975	0.9874	0.9747	0.9485	0.8930	0.8323	0.7649	0.6880
1.15	0.9978	0.9891	0.9780	0.9554	0.9081	0.8576	0.8032	0.7443
1.20	0.9981	0.9904	0.9808	0.9611	0.9205	0.8779	0.8330	0.7858

$Z^0 = \frac{0.800-0.659}{0.8-0.6} \times 0.8779 + \frac{0.659-0.600}{0.8-0.6} \times 0.8330 = 0.865$

$Z^1 = \frac{0.800-0.659}{0.8-0.6} \times 0.0326 + \frac{0.659-0.600}{0.8-0.6} \times 0.0499 = 0.038$

$Z = Z^0 + \omega Z^1 = 0.865 + 0.2 \times 0.038 = 0.8726$

a.) Ideal Gas: $V = \frac{RT}{P} = \frac{8.314 J \cdot mol^{-1} \cdot K^{-1} \times 510K}{25 bar} = 1696.1 cm^3 \cdot mol^{-1}$

b) The Pitzer correlation: $V = \frac{ZRT}{P} = \frac{0.8726 \times 8.314 J \cdot mol^{-1} \cdot K^{-1} \times 510k}{25bar} = 1480.7 cm^3 \cdot mol^{-1}$

Lecture 4

4 HCl(g) + $O_2(g)$ → 2 H_2O(g) + 2 Cl_2 (g) takes place at temperature 25°C at 1 bar.
What is the standard reaction enthalpy?

$\Delta H_r^\circ = 2 * \Delta H_{f,H_2O}^\circ + 2 * \Delta H_{f,Cl_2}^\circ - 4 * \Delta H_{f,HCl}^\circ - \Delta H_{f,O_2}^\circ$

$= 2 * \left(-241818 \frac{J}{mol}\right) + 2 * 0 - 4 * \left(-92307 \frac{J}{mol}\right) - 0 = -114408 \frac{J}{mol}$ (exothermic)

单质 ΔH° 为 0

Standard reaction Enthalpy: Table C.4

Table C.4 (Continued)

Chemical species		State (Note 2)	ΔH_{f298}° (Note 1)	ΔG_{f298}° (Note 1)
Miscellaneous inorganics:				
Ammonia	NH_3	(*g*)	−46,110	−16,400
Ammonia	NH_3	(*aq*)		−26,500
Calcium carbide	CaC_2	(*s*)	−59,800	−64,900
Calcium carbonate	$CaCO_3$	(*s*)	−1,206,920	−1,128,790
Calcium chloride	$CaCl_2$	(*s*)	−795,800	−748,100
Calcium chloride	$CaCl_2$	(*aq*)		−8,101,900
Calcium chloride	$CaCl_2 \cdot 6H_2O$	(*s*)	−2,607,900	
Calcium hydroxide	$Ca(OH)_2$	(*s*)	−986,090	−898,490
Calcium hydroxide	$Ca(OH)_2$	(*aq*)		−868,070
Calcium oxide	CaO	(*s*)	−635,090	−604,030
Carbon dioxide	CO_2	(*g*)	−393,509	−394,359
Carbon monoxide	CO	(*g*)	−110,525	−137,169
Hydrochloric acid	HCl	(*g*)	−92,307	−95,299
Hydrogen cyanide	HCN	(*g*)	135,100	124,700
Hydrogen sulfide	H_2S	(*g*)	−20,630	−33,560
Iron oxide	FeO	(*s*)	−272,000	
Iron oxide (hematite)	Fe_2O_3	(*s*)	−824,200	−742,200
Iron oxide (magnetite)	Fe_3O_4	(*s*)	−1,118,400	−1,015,400
Iron sulfide (pyrite)	FeS_2	(*s*)	−178,200	−166,900
Lithium chloride	LiCl	(*s*)	−408,610	
Lithium chloride	$LiCl \cdot H_2O$	(*s*)	−712,580	
Lithium chloride	$LiCl \cdot 2H_2O$	(*s*)	−1,012,650	
Lithium chloride	$LiCl \cdot 3H_2O$	(*s*)	−1,311,300	
Nitric acid	HNO_3	(*l*)	−174,100	−80,710
Nitric acid	HNO_3	(*aq*)		−111,250
Nitrogen oxides	NO	(*g*)	90,250	86,550
	NO_2	(*g*)	33,180	51,310
	N_2O	(*g*)	82,050	104,200
	N_2O_4	(*g*)	9,160	97,540
Sodium carbonate	Na_2CO_3	(*s*)	−1,130,680	−1,044,440
Sodium carbonate	$Na_2CO_3 \cdot 10H_2O$	(*s*)	−4,081,320	
Sodium chloride	NaCl	(*s*)	−411,153	−384,138
Sodium chloride	NaCl	(*aq*)		−393,133
Sodium hydroxide	NaOH	(*s*)	−425,609	−379,494
Sodium hydroxide	NaOH	(*aq*)		−419,150
Sulfur dioxide	SO_2	(*g*)	−296,830	−300,194
Sulfur trioxide	SO_3	(*g*)	−395,720	−371,060
Sulfur trioxide	SO_3	(*l*)	−441,040	
Sulfuric acid	H_2SO_4	(*l*)	−813,989	−690,003
Sulfuric acid	H_2SO_4	(*aq*)		−744,530
Water	H_2O	(*g*)	−241,818	−228,572
Water	H_2O	(*l*)	−285,830	−237,129