Chemical Engineering Thermodynamics
COURSE PROJECT

ISENTROPIC HEAT AND EXCESS FREE ENERGY CALCULATIONS FOR N2 INDUCED **EOR** (ENHANCED OIL RECOVERY)

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Aim :

To study the properties of Enhanced Oil Recovery via Fracking using Liquid Nitrogen(N2)

Objective :

1) To explain how the excess free energy varies with temperature and pressure in each range.

2) To show how the isentropic heat change(ΔT) varies with temperature and pressure within each range during the fracking process.

3) To discuss how these thermodynamic properties impact the efficiency and effectiveness of the fracking process.

Theory :

Enhanced Oil Recovery Using Liquid Nitrogen:
- **Gas Mobility Control:** Nitrogen is an inert gas, which means it doesn't react with the oil or reservoir rock. Injecting nitrogen into an oil reservoir helps to displace oil by reducing its viscosity and improving its mobility. This can be especially useful in reservoirs where the oil is heavy or highly viscous.Nitrogen gas is much cheaper and more easily to obtain as it is abundant in air(78%).

- **Pressure Maintenance:** As oil is extracted from a reservoir over time, the reservoir pressure decreases. This pressure decline can make it increasingly challenging to extract more oil. Nitrogen injection can help maintain or even increase the reservoir pressure, which, in turn, can improve oil recovery rates. The elevated pressure can push oil towards the production wells.

- As a fracturing fluid, LN2 greatly reduces the expansion of reservoir clay and the water lock effect. Unlike traditional hydraulic fracturing(basically means extraction from wells), LN2 fracturing produces no wastewater or water pollution.

- The injection of ultralow temperature (−196 °C) LN_2 into coal rock effectively changes the coal rock mechanical properties, reduces fracture pressure, and increases the width of primary fractures in the reservoir.

- Low-temperature LN_2 enters the coal rock, induces the formation and expansion of secondary fractures in the coal rock, enhances pore connectivity, improves the pore structure of the coal rock, and provides channels for unconventional oil and gas migration.

As the share of unconventional oil and gas in global oil and gas production gradually increased, the amount of research on LN_2 fracturing has also increased. Figure shows the number of research articles on LN_2 fracturing published between 2011 and 2021.

https://pubs.acs.org/doi/full/10.1021/acs.energyfuels.2c00084
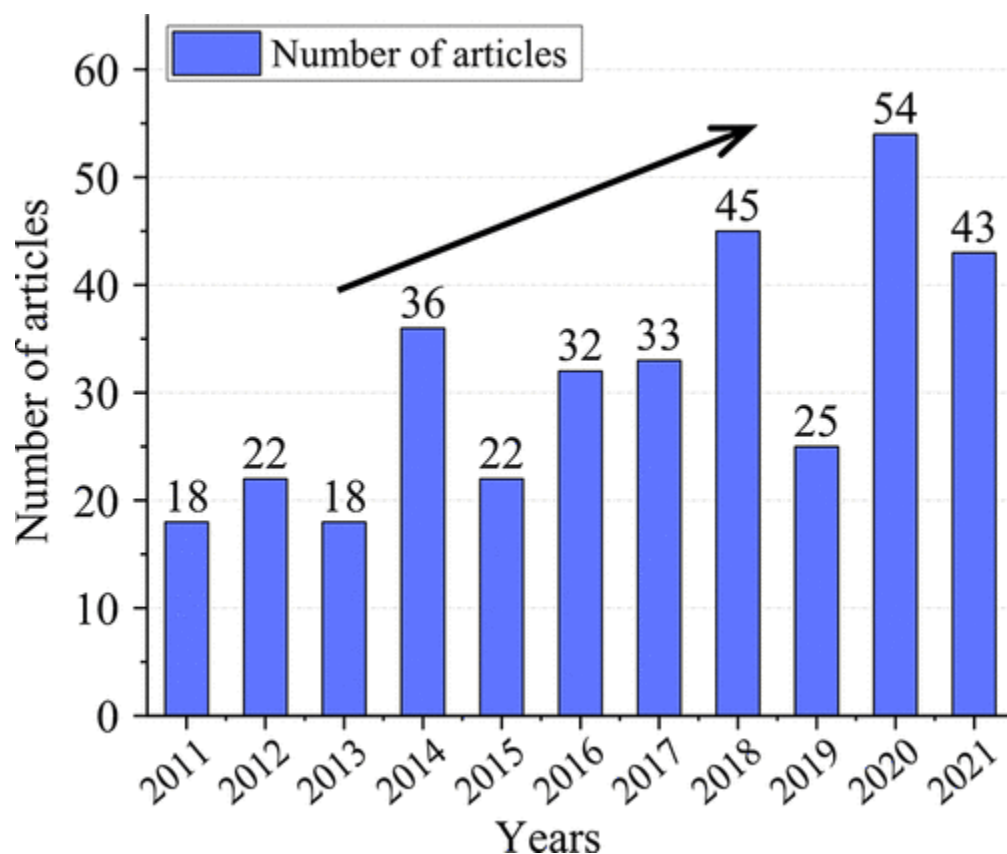
Calculations and Observations:

1) To find the excess free energy

Using Redlich Kwong Equation

P = RT/(V-b) - a/(sqrt(T)*V*(V+b))

where:

- p is the gas pressure(Mpa)
- R is the gas constant(J/k-mol),
- T is temperature(K),
- V is the molar volume (V/n),
- a = 0.42748R^2*Tc^(2.5)/Pc
- b = 0.08664*R*Tc/Pc
- Tc= 126.21K
- Pc= 3.4 Mpa

Using Maxwell Equation

dU = dQ-PdV

dG = -SdT + VdP , where (G = H - TS)

At constant Temperature.

dG = VdP

dG = RT*dP/P = RT*dln(P)

dG^{ig} = RTd(ln(P))   -   (1)

dG = RTd(ln(f))   -   (2)   , where f = fugacity

Therefore for ideal gas f = P

On subtracting (1) from (2)

d(G - G^{ig}) = RTd(ln(f/P)) = RTdlnϕ , where ϕ = fugacity coefficient

dG^R = d(G-Gig)

$d(G^R/RT)$ = d(ln(ϕ))

d(ln(ϕ)) = (dG - dGig)/RT = (VdP - Vig*dP)/RT

d(ln(ϕ)) = (V- Vig)dP/RT

d(ln(ϕ))=[Vdp - Vigdp]/RT

　　　　=[d(PV) - Pdv - Vig*dP]/RT

　　　　=[d(PV/RT) - P/RTdv - (Vig/RT)dP]

Now from RKE Equation,

　　　　= d(z) - (dv/V-b) + (adv/sqrtT*V*(V+b)) - (Vig/RT)dP

　　　　= d(z) - (dv/V-b) + a/RTsqrt(T)*b[dv/V - dv/V+b] - (Vig/RT)dP

A = aP/(sqrt(T)*(RT)^2) , B = bP/RT

d(ln(ϕ)) = dz - dv/(V-b) + (A/B)*(dv/V - dV/(V+b)) - d(ln(P))

Initially gas is ideal hence ϕ = 1 as ϕ = f/P and for ideal gas f=P

On integrating the above equation we get

ln(ϕ) = (z-1) - ln((V-b)/(Vig - b)) + (A/B)*{ln(V/Vig) - ln[(V+b)/Vig]}

Now to put V=ZRT/P

ln(ϕ) = (Z-1) - ln((ZRT/P - b)/RT/p) + (A/B)ln(V/V+b)

After simplifying,

ln(ϕ) = (Z-1) - ln(Z - B) + (A/B)ln(Z/Z+B)　　　- eq(3)

Now to find value Z at particular pressure and temperature , change the RKE in terms of

Z and simplify it,

Put V = ZRT/P in RKE,

P = RT/(ZRT/P - b) - a/(sqrt(T)ZRT/P)*(ZRT/P + b)

P = PRT/(ZRT - Pb) - aP^2/(sqrt(T)ZRT(ZRT+Pb)

After simplifying, we get

A = aP/(sqrt(T)*(RT)^2) , B = bP/RT

A = 0.42748*(Tc)^(2.5) * P/(T^(2.5)*Pc) , as   a = 0.42748*R^2Tc^(2.5)/Pc

B = 0.08664*Tc*P/(Pc*T)   , as   b = 0.08664*R*Tc/Pc

1 = 1/(z-B) - A/(z*(z+B))

After solving the above equation we get

z^3 - z^2 + z(A-B-B^2) - AB = 0   - eq(4)

Calculation Table:

Temp	P(MPa)	A	B	Z	Z1	LNPhi	Gr
312.61	52	0.677123	0.534975	1.317876	1.317876	0.131393	341.4957
312.61	55	0.716188	0.565839	1.348703	1.348703	0.150077	390.0572
312.61	60	0.781296	0.617279	1.400733	1.400733	0.182644	474.6993
312.61	65	0.846404	0.668719	1.453383	1.453383	0.216795	563.46
312.61	70	0.911512	0.720159	1.506486	1.506486	0.252336	655.8308
322.19	62	0.748657	0.618889	1.411831	1.411831	0.204115	546.7595
322.19	65	0.784882	0.648835	1.442347	1.442347	0.224289	600.8014
322.19	68	0.821108	0.678782	1.473028	1.473028	0.244935	656.1039
322.19	70	0.845258	0.698746	1.493568	1.493568	0.258943	693.6271
322.19	75	0.905633	0.748656	1.545134	1.545134	0.294752	789.5494
331.77	72	0.807999	0.697957	1.501362	1.501362	0.278291	767.6208
331.77	75	0.841666	0.727039	1.531295	1.531295	0.299364	825.7473
331.77	78	0.875333	0.75612	1.561325	1.561325	0.320787	884.8379
331.77	80	0.897777	0.775508	1.581392	1.581392	0.335251	924.7356
331.77	82	0.920221	0.794895	1.60149	1.60149	0.349854	965.016
341.35	82	0.857009	0.772587	1.586224	1.586224	0.352304	999.8332
341.35	84	0.877912	0.79143	1.605708	1.605708	0.366664	1040.588
341.35	85	0.888363	0.800852	1.615461	1.615461	0.37389	1061.094
341.35	86	0.898814	0.810274	1.625219	1.625219	0.381146	1081.685
341.35	88	0.919717	0.829117	1.644755	1.644755	0.395743	1123.111
350.93	91	0.887486	0.833977	1.657014	1.657014	0.417949	1219.421
350.93	91.5	0.892362	0.83856	1.661758	1.661758	0.421562	1229.963
350.93	92	0.897238	0.843142	1.666504	1.666504	0.425181	1240.522
350.93	92.5	0.902115	0.847724	1.671252	1.671252	0.428807	1251.1
350.93	93	0.906991	0.852306	1.676	1.676	0.432438	1261.695

Graph

Excess Free Energy vs Pressure
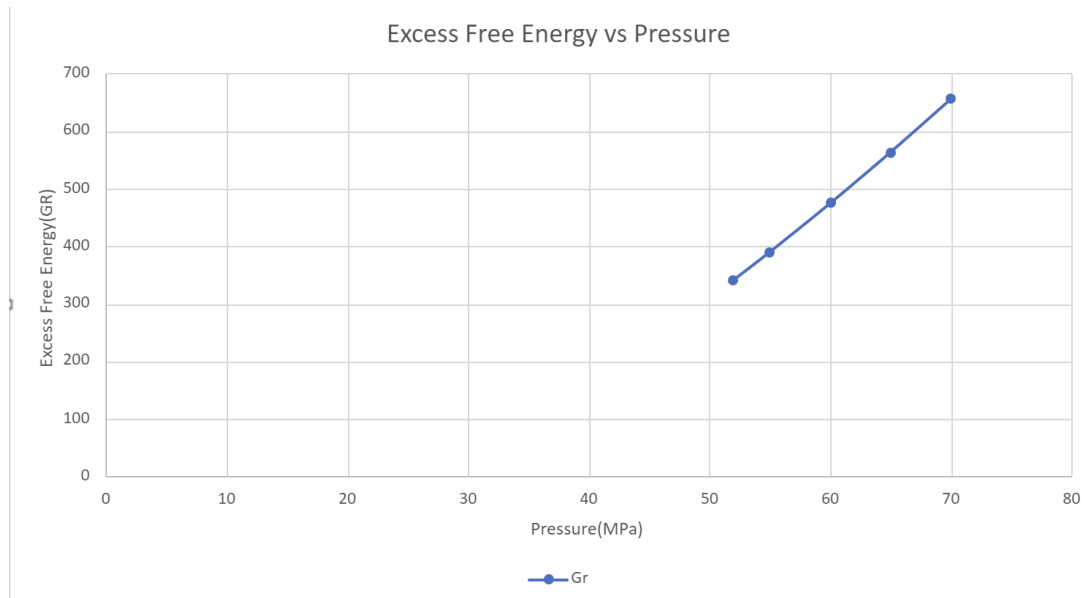
Graph is between Excess Free Energy(G^E) vs Pressure(MPa)

Conclusions:

- As we can see from the graph, the G^E is increasing with increasing pressure at constant temperature. And we can see from the calculation table also as Z is increasing there is an increase in excess free energy. It suggests that the system is becoming less stable at higher pressures.

- This increase in excess free energy implies that the system is deviating further from its equilibrium state, which can have various implications depending on the specific conditions and components involved. It might indicate a tendency for phase transitions or other changes in the system's behavior.

2) <u>To find the Isentropic heat change (ΔT):</u>

The process is given to be isentropic. Therefore, **ΔS = 0**.
Since the Nitrogen used is in its liquid state, the following equation is used for it's entropy:-

$$dS = C_p.(dT/T) - \beta VdP$$

β = Volume expansivity, Cp= Specific Heat and V= Volume of Liquid

This equation incorporating β, although general, is usually applied only to liquids
Here, it is also considered to be a real fluid and thus, cannot be considered to be incompressible which can eliminate the beta and volume terms. They have to be taken into consideration as well.

As we can see from our calculations and even in general, β and V are weak functions of pressure for liquids, they are usually assumed constant at appropriate average values for integration of the final terms. Therefore, entropy can be written as

$$\Delta S = \langle C_p \rangle.\ln(T_2/T_1) - \langle \beta \rangle \langle V \rangle (P_2 - P_1) = 0$$

Since β=(dV/dT)/Vo, in order to find dV, an approximation for the final volume and temperature is needed if β is to be found for varying ranges of pressure in our case.

Therefore, to get an approximate value of final temperature , an ideal condition can be assumed to get the value of β to then calculate the real/actual values afterwards.

$$(T_2/T_1)=(P_2/P_1)^{(1-1/k)}$$

The above equation can be used to calculate an approximate value of T2 in order to find β for our final calculations

After getting the approximate values of final temperature, The Redlich-Kwong equation of state(which is given above) can be used to calculate both the initial and final molar volumes of Nitrogen.
The values obtained are then used to find the values of β for all the given temperature and pressure ranges using:

$$\beta=-(dV/dT)/V_o$$

Now, using the above obtained entropy formula and equating it to zero, we get

$$T2 = T1 * \exp[\langle\beta\rangle\langle V\rangle(P2{-}P1) / \langle Cp\rangle]$$

$$\therefore \quad \Delta T = T1 - T2 = T1 * (1 - \exp[\langle\beta\rangle\langle V\rangle(P2{-}P1) / \langle Cp\rangle] \;)$$

Calculation Table:

T1	P1	P2			T2(ideal)	ΔT(ideal)	v1(cm3/m)	v2	vg Cp(liquid)	β	Avg V(cm3)			T2(actual)	ΔT(actual)
312.61	70	65			306.0605	6.549529	55.9365	57.2113	1950	0.00348	56.5739			307.0256	5.584442
312.61	65	60			305.5419	7.068057	58.1161	59.6091		0.003635	58.8626			306.5456	6.064444
312.61	60	55			304.9342	7.6758	60.6785	62.4544		0.003813	61.56645			305.9622	6.647833
312.61	55	52			307.6402	4.969822	63.7361	64.9877		0.003951	64.3619			308.2727	4.337346
312.61	70	52			287.1565	25.45349	55.9365	61.349		0.003802	58.64275			290.4613	22.14868
322.19	75	70			315.9011	6.288902	55.1877	56.3551		0.003364	55.7714			316.703	5.486987
322.19	70	68			319.5326	2.657407	57.1563	57.6782		0.003436	57.41725			319.8702	2.319763
322.19	68	65			318.0631	4.126871	58.0285	58.8701		0.003514	58.4493			318.5745	3.615515
322.19	65	62			317.8694	4.320599	59.4422	60.3675		0.003603	59.90485			318.3922	3.797774
322.19	75	62			305.1351	17.05489	55.1877	58.5113		0.003531	56.8495			307.1542	15.03576
331.77	82	80			329.4376	2.332411	53.873	54.2694		0.003155	54.0712			329.7037	2.066317
331.77	80	78			329.3787	2.391252	54.5269	54.9437		0.003197	54.7353			329.6507	2.119326
331.77	78	75			328.073	3.697034	55.2154	55.8738		0.003225	55.5446			328.5206	3.2494
331.77	75	72			327.9229	3.847096	56.3196	57.0431		0.003339	56.68135			328.338	3.432027
331.77	82	72			319.6683	12.10169	53.873	56.0223		0.003297	54.94765			320.9446	10.82542
341.35	88	86			339.1152	2.234787	53.0446	53.4055		0.003044	53.22505			339.3301	2.019899
341.35	86	85			340.2112	1.138794	53.6336	53.8211		0.00307	53.72735			340.3205	1.029487
341.35	85	84			340.1978	1.152249	53.9387	54.1301		0.00308	54.0344			340.3114	1.038643
341.35	84	82			339.0079	2.342128	54.2514	54.6481		0.003122	54.44975			339.2313	2.118739
341.35	88	82			334.5318	6.818215	53.0446	54.1687		0.003108	53.60665			335.1576	6.192356
350.93	93	92.5			350.3899	0.540101	52.5817	52.6643		0.002909	52.623			350.4385	0.491467
350.93	92.5	92			350.387	0.543026	52.7161	52.8		0.002931	52.75805			350.4335	0.496514
350.93	92	91.5			350.384	0.545983	52.8521	52.9371		0.002946	52.8946			350.4297	0.500301
350.93	91.5	91			350.381	0.548973	52.9895	53.0758		0.002967	53.03265			350.4248	0.505189
350.93	93	91			348.757	2.173019	52.5817	52.9196		0.002957	52.75065			348.9306	1.999358

(Here, the rows highlighted in blue represent the values for the largest change in pressure possible for the selected initial temperature)

Graph:

ΔT vs T1 for Maximum possible pressure difference
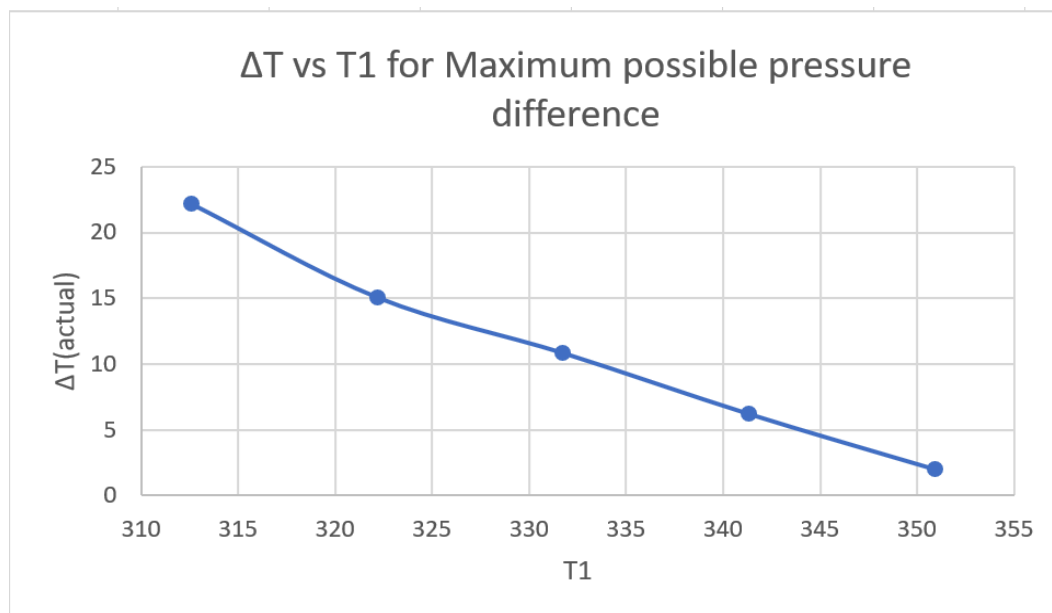
Conclusions:

Front the above calculations, table and graph it can be observed that:

i) w.r.t Pressure, For similar **ΔP** at the constant initial temperature **(T1)** , **ΔT** increases as **P1** (i.e. initial pressure) decreases. **ΔV** also seems to increase for the same.

ii) w.r.t Temperature, As seen in the graph above, for the maximum range of pressure difference possible at a select initial temperature, **ΔT** decreases as **T1** increases. (Highlighted in blue). **ΔV** sees a noticeable decline in this case.

Thus, simply increasing the temperature for the given ranges of operating pressures for each of them doesn't guarantee a greater expansion of liquid Nitrogen under isentropic conditions and is actually the opposite in the given case study. For the same range of **ΔP** at the same temperature though, a decrease in the initial pressure seems to result in greater expansion of liquid Nitrogen(LN2).

3) Significance of the above calculated values:

- In fracturing operations, stability and predictability are typically desirable. An increase in excess free energy might indicate that the conditions are approaching a point where the nitrogen fracturing process may become less efficient or less controllable. Therefore, from an operational perspective, an increase in excess free energy with increasing pressure is often not considered beneficial and might require adjustments to maintain process integrity and efficiency.

- Increasing the temperature can also increase the thermal stress around the hole causing damage and can even lower the viscosity of the liquid which can further affect the process of fracking itself. In some cases, gaseous N2 may also be formed, which is also not desirable.